

## **REMARKS/ARGUMENTS**

The examiner has rejected claims 1-12 and 14-39 under the judicially created doctrine of obviousness-double patenting as being unpatentable over claims 1-7 and claims 1-23 of U.S. patent nos. 6,342,110 and 6,592,686 respectively. The examiner also rejects claims 1-12, 14-23, 26 and 31-39 under the judicially created doctrine of obviousness-double patenting as being unpatentable over claims 1-7 and 1-3 of U.S. patent no. 6,086,691.

Applicant submits that the above obviousness-double patenting rejections may be overcome by filing a terminal disclaimer. However, since the examiner has rejected all of the claims on the basis of other prior art under 35 U.S.C. § 102 and/or 103, it is clear that there is no indication of allowable subject matter at the present time. Without an indication of allowable subject matter, there is no basis to conclude that issuance of a patent will unjustly extend the patent rights of the patents and/or applications which form the basis of the obviousness-double patenting rejection. Thus, applicant submits that any requirement for a terminal disclaimer at the present time is premature. Accordingly, applicant respectfully requests the examiner to hold the obviousness type double patenting rejection in abeyance until there is at least an indication of allowable subject matter.

In addition, applicant submits that the obviousness type double patenting rejections are no longer available to the presently amended claims. Accordingly, applicant respectfully requests the examiner to reconsider these rejections in view of the presently amended claims.

In response to these rejections, applicant submits herewith a terminal disclaimer with respect to the three cited U.S. patents.

The examiner has rejected claims 1-12, 14-27, 29 and 31-39 under 35 U.S.C. § 102(b) as being anticipated by or, alternatively, under 35 U.S.C. § 103(a) as being obvious over JP 06-267544 (Yasuda). In rejecting the claims the examiner urges that Yasuda discloses cold working a Pb-Sn-Ca alloy at 120°C or less and recrystallizing the cold worked alloy at a temperature of 60° or more. The examiner argues that the above-noted steps of the cited reference will result in the recrystallized lead or lead alloy of applicant's invention. The examiner acknowledges, however, that the cited reference does not disclose the various plastic deformation methods, cycles of cold work and recrystallization annealing and the amount of special grain boundaries. Nonetheless the examiner urges that the reference anticipates the claimed invention because a product is being claimed, not a process. Applicant has carefully considered this rejection but it is most respectfully traversed for the reasons discussed below.

Before discussing the rejection, applicant first wishes to emphasize that the gist of the present invention is the manipulative steps which are required to produce a minimum content of special grain boundaries. While various types of recrystallization procedures are known to the art, and many alloys are recrystallized such as the alloy of the cited reference, not all recrystallized alloys will have the same properties, in particular, not all recrystallized alloys will have the minimum content of special grain boundary fraction of applicant's invention. The objective of applicant's invention is to maximize the fraction of special grain boundaries (i.e., maximize the Fsp fraction) not merely to recrystallize the alloy since, not all recrystallization will lead to applicant's objective.

In order to emphasize the above-noted objective of applicant's invention which is to maximize the Fsp fraction, applicant has amended the claims by removing the reference to recrystallizing the alloy. The claims now focus on an

alloy having a minimum percentage of special grain boundaries (20% in claim 1 and higher amounts in other claims). In this regard the examiner acknowledges that the cited reference does not disclose the amount of special grain boundaries required by applicant's invention. Applicant submits that the mere occurrence of recrystallization as described in the cited reference, is not sufficient to conclude that the recrystallization is of the particular type and extent which results in applicant's objective of a minimum special grain boundary content.

In addition, all of applicant's claims require an annealing step after the initial deformation step wherein the annealing takes place at a temperature between 100°C and the melting point of the lead or lead alloy. It will be apparent from the discussion below that one skilled in the art will understand from the description of Yashuda that the heating step which Yashuda uses and which the examiner considers to be the same as applicant's annealing step, must take place at a temperature below the boiling point of water (i.e., below 100°C) which is less than the minimum temperature required in applicant's invention.

Yashuda describes a process for casting a Pb-Ca-Sn slab followed by a laminating procedure in which the slab is laminated to a Pb-Sb-Sn strip in a cold rolling laminating procedure (at 120°C or less) whereby a laminated strip is formed from these two materials [0018]. Next the laminated strip is expanded to form a mesh and then the mesh is pasted with active material followed by a heat-treatment (drying) at 60°C or more. The sole purpose of the heat treatment step is **to improve the grid-paste adhesions** [0020 and drawing 2]. The Sb containing surface layer is credited for providing the improved paste/grid adhesion.

As observed by the examiner, Yashuda is not concerned with the same process of applicant's invention; however the examiner asserts that Yashuda's grids are substantially identical to the grid of applicant's invention. Applicant submits that this is not the case for the reasons discussed below.

Yashuda's laminate contains a Pb-0.05-0.08 Ca-0.5-2.0 Sn and a Pb-5.0 Sb-5.0 Sn layer formed by a rolling process, during which the thickness is reduced from 1 cm to 1 mm (90% rolling reduction) [0017, drawing 1]. The rolling occurs at up to 120°C to aid in the fusion between the Pb-Ca-Sn and the Pb-Sb, Sn laminate layers. The laminate strip is aged at **60°C for two days** presumably to age harden the strip to achieve the desired strength required for expansion [0021].

The laminate strip of Yashuda is subsequently expanded into a mesh and pasted with active material. Yashuda then goes on to state that the strip had a wrought structure and after filling the mesh with the paste, part of the grid recrystallizes in the **heat treatment, which is defined as 60°C for 48 hours** [0010].

In view of the above, it is clear that Yashuda applies two heat treatments to the strip after the initial cold rolling at 120°C or less. The first heat treatment is performed on the **unpasted** strip before expansion. This heat treatment is conducted at 60°C for two days. It is to be noted that no other information is provided on the temperature requirements for this first heat treatment step other than heat treatment at exactly **60°C for two days**. It is therefore clear that this heat treatment step does not correspond to applicant's annealing step which requires a minimum temperature of 100°C.

The second heat treating step used by Yashuda after the initial cold rolling is performed on the **pasted plate**. This second heat treating step takes place at a temperature of 60°C or higher. Presumably the examiner considers this second heat treating step to be comparable to applicant's annealing step which requires a minimum temperature of 100°C apparently because the examiner considers a teaching of "60°C or higher" to mean that Yashuda teaches any temperature above 60°C. Applicant submits that one skilled in the art will understand from the teaching of Yashuda that not all temperatures above 60°C are appropriate for heating treating the paste/metal combination. In particular, one skilled in the art will understand that Yashuda does not contemplate using temperatures above 60°C which will interfere with the desired characteristics of the paste which is on the metal during this second heat treating step. Such temperatures which will interfere with the paste are temperatures which adversely affect the curing process of the water based paste used by Yashuda. In this regard it is to be noted that Yashuda forms the paste by kneading paste components with water and dilute sulfuric acid [0021].

It is well known to those skilled in the art that the maximum temperature for treating a pasted grid such as the pasted grid of Yashuda, is limited to below 100°C. In particular, it is well known to those skilled in the art that the curing process of pasted plates takes place at 60° to 95°C which accounts for Yashuda's statement of 60° or higher. Clearly, by reference to temperatures higher than 60°, Yashuda is only referring to temperatures which lie within the known range for heat treating such pasted plates, not temperatures which exceed this amount. It is well known to those skilled in the art that the pasted plate should not be heated to 100°C (the boiling point of water) or higher to avoid water loss from the paste and to avoid cracking due to shrinkage. Support for the maximum heat treatment temperature of paste and pasted grids is found in Lead Acid Batteries

(H. Bode, John Wiley and Sons, 1977). A copy of the relevant portion of this publication is enclosed herewith.

In view of the above, it is clear that Yashuda's teaching of "60° or higher" will be understood to those skilled in the art as not including all temperatures higher than 60°C which are achievable, but rather will be understood as being limited to 60°C and higher temperatures **which do not exceed the maximum temperature to which a pasted plate may be exposed**. Since this maximum temperature is 95°C as noted above, it therefore follows that one skilled in the art will understand that although Yashuda indicates temperatures higher than 60°, such higher temperatures will be understood by those skilled in the art as being less than the minimum temperature of 100°C of applicant's invention.

In view of the above it is clear that one skilled in the art will understand that if Yashuda's plates are treated in the temperature range of applicant's invention, such a heat treatment of the pasted plates would render them unsuitable for use in lead acid batteries. In this regard the examiner's attention is directed to the attached article by J.R. Pierson (Power Sources 2, 1970, pp. 103-119) which defines the "high temperature curing" temperature as greater than 150°F (66°C) and which demonstrates that plates cured at 180°F (82°C) result in only about 50% conversion of the paste to PbO<sub>2</sub> active material and yields on conversion the alpha-PbO<sub>2</sub> rather than the desired beta-PbO<sub>2</sub>. Moreover, during operation/cycling, additional sulphate would be released from the center of the plate yielding uneven electrolyte gravity conditions and significant cell-to-cell variations. The reduction in useful discharge capacity to half the nominal value and other deficiencies noted above were verified in actual battery tests as well (see Pierson page 117).

It is also to be noted that the grain boundary engineered grids produced in accordance with applicant's invention are used in the production of batteries and would therefore be pasted and processed. In other words the grid containing the special grain boundaries would be subjected to pasting, drying and curing steps. Furthermore, when the engineered grid has the special grain boundary fraction produced in accordance with applicant's invention, any processing of the pasted plates would be conducted under conditions which would not alter the special grain boundary fraction which applicant requires. Clearly, if the curing/drying heat treatment of Yashuda is sufficient to obtain a Fsp greater than 20%, there would be no need for applicant to add an additional heat treating step after the initial deformation, since the drying heat treating step of Yashuda would be sufficient to establish this Fsp characteristic. However, this is clearly not the case. Thus it is self-evident that there is no basis to conclude that Yashuda leads to the Fsp content recited in applicant's claims.

Yashuda further states that recrystallization treatment of the Pb-Ca-Sn alloy **improves the mechanical properties** [0014]. However, it is noted in applicant's specification that applying the grain boundary engineering process of applicant's invention diminishes the mechanical properties. Note particularly example 4, table 2 which demonstrates the reduced mechanical strength of grain boundary engineered Pb-alloys, including a Pb-0.08 Ca-1.2Sn alloy, quite similar to the Pb-0.07 Ca-1.0Sn alloy processed by Yashuda, which dropped from 20.8 to 13 Hv after grain boundary engineering. **Thus, it is clear that although Yashuda produces recrystallization, his recrystallization is clearly different from the recrystallization associated with the improved grain boundary engineering of applicant's invention.**

Serial No. 09/991,702

In view of the above, applicant submits that claims 1-12, 14-27, 29 and 31-39 are not anticipated nor are they obvious over Yashuda.

In addition to the above argumentation, applicant further submits that claims 23, 24 and 26-39 are additionally distinguished over Yashuda for the reasons discussed below.

Dependent claim 23 requires a deformation of 1-70%, which is clearly outside of Yashuda's applied deformation of 90%.

Independent claim 24 requires a deformation of 10-40%, which is clearly outside of Yashuda's applied deformation of 90%.

Dependent claim 26 requires a deformation of 20% in 6 cycles, which is outside of Yashuda's applied deformation of 90% in a single cycle.

Dependent claim 27 requires a deformation of 40% in 3 cycles, which is outside of Yashuda's applied deformation of 90% in a single cycle.

Dependent claim 29 requires a deformation of 40% in 2 cycles which is clearly outside of Yashuda's applied deformation of 90% in a single cycle.

Dependent claims 31-39 depend from claim 12 and thereby include the step of **extruding the billet to a strip of desired thickness while maintaining the strip at a temperature up to the solvus temperature of the lead or lead alloy and optionally quenching the strip**. Clearly, Yashuda does not even remotely disclose or suggest this extrusion step of claims 31-39.



It is also to be noted that applicant requires a step where the metal is deformed at a temperature up to the solvus temperature of the lead or lead alloy. The closest Yashuda comes to disclosing such a deformation step is the step of "cold rolling the slab" mentioned in [0009]. Thus, Yashuda does not disclose or suggest extrusion, bending, peening etc. for deforming the metal and thus claims which require deformation processes which are different from the "rolling" required by Yashuda are clearly patentably distinct over this reference. Thus, for example, claim 38 which requires deformation by "peening" is clearly patentably distinct over Yashuda.

The examiner has rejected claims 28 and 30 under 35 U.S.C. § 103(a) as being unpatentable over Yashuda and further in view of Rao. In addition the examiner has rejected claim 28 under 35 U.S.C. § 103(a) as being unpatentable over Yashuda and further in view of DE2758940. In rejecting the claims the examiner urges that Yashuda teaches all the elements of the claims except for the Ag content. The examiner turns to the teaching of Rao or DE2758940 for the teaching of the Ag content. Applicant has carefully considered these rejections but they are most respectfully traversed for the reasons discussed below.

As discussed above, Yashuda fails to disclose or suggest applicant's annealing step which requires a minimum temperature of 100°C. Neither of the secondary references compensate for this deficiency. Accordingly, using the Ag content of the secondary references in the alloy of Yashuda will not result in applicant's claimed invention.

In addition, claim 28 requires a deformation of 40% in two cycles, which is clearly outside of Yashuda's applied deformation of 90% in a single cycle.

Serial No. 09/991,702

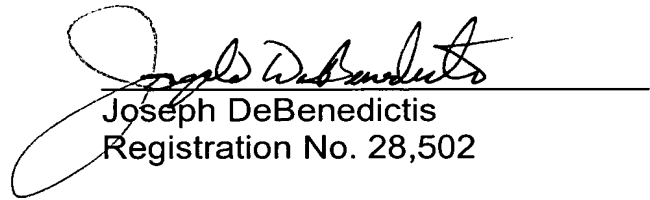
Neither of the secondary references compensate for this deficiency of Yashuda.

Claim 30 requires a 20% reduction which is clearly outside of Yashuda's applied deformation of 90%. Neither of the secondary references compensate for this deficiency of Yashuda. In addition, claim 30 requires a Ag content of 0.6% whereas Rao teaches 0.015 to 0.045%-Ag.

In view of the above arguments and amendments, applicant respectfully requests reconsideration and allowance of all the claims which are currently pending in the application.

Respectfully submitted,  
**BACON & THOMAS, PLLC**

Date: May 13, 2004



Joseph DeBenedictis  
Registration No. 28,502

**BACON & THOMAS**  
625 Slaters Lane, 4th Floor  
Alexandria, Virginia 22314  
Telephone: (703) 683-0500

S:\Producer\jdb\Ridout & Maybee\Palumbo Aust 991702\Amend 05.wpd

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

## A STUDY OF SOME OF THE CRYSTALLOGRAPHIC AND MICROSCOPIC ASPECTS OF THE CURING OF POSITIVE LEAD-ACID BATTERY PLATES

JOHN R. PIERSON

Globe Battery Division, Globe-Union Inc., Milwaukee, Wisconsin, U.S.A.

### ABSTRACT

The process of curing or conditioning pasted lead-acid battery plates made with uncalcined or leady Barton pot litharge is probed. Microscopy, wet chemistry and X-ray diffraction techniques are used to characterize the changes in crystal structure and chemical composition which take place in the material as it undergoes curing.

A matched set of uncured positive plates is divided into groups each of which is then cured under different controlled conditions. At various times throughout the cure cycle, sample plates from each group are analyzed for composition and crystal structure. Photomicrographs used in conjunction with X-ray diffraction patterns illustrate the reactions which occur.

The plates cured under various conditions are then formed or charged. Time-lapse photographic techniques are used to follow the conversion of divalent lead compounds into the various species of lead dioxide. The degree of completion of formation and the proportions and characteristics of the two polymorphs of lead dioxide present in the formed plates of varying cure history are discussed.

### INTRODUCTION

Interest in the crystallographic nature of the positive and negative active material in lead-acid battery plates has been stimulated in recent years by the extremely interesting and comprehensive reports generated at the U.S. Naval Research Laboratory. The microscopic studies of A. C. Simon and the X-ray diffraction techniques of J. Burbank are particularly noteworthy. The publications released by these researchers have proven to be invaluable references for anyone seriously interested in investigating the crystallographic characteristics at various stages of battery plate processing and life. Much of the work reported upon in this paper had its origin in findings published by NRL personnel.

### BACKGROUND

Uncalcined or leady litharge has been utilized in the manufacture of paste for lead-acid battery plates for 25 years or more. This material,

commonly called battery oxide, grey oxide or lead dust, is generally made by one of two processes: the ball mill process or the Barton pot process. The "oxide" which results typically contains about 75 per cent lead monoxide which appears as either of two polymorphs (tetragonal and orthorhombic). The remaining 25 per cent by weight is unoxidized metallic lead in the form of finely divided particles.

The "oxide" is mixed with water, dilute sulfuric acid and various lesser additives to make a paste which is then applied to cast lead alloy grids. After flash drying, the plates are normally stacked or racked in some manner and allowed to age or cure prior to electrochemical formation or charging. In curing, the plates are dried and strengthened and, hence, prepared mechanically for subsequent handling and formation. The reactions which occur during this aging or curing process and the changes in crystal structure and chemical composition which can result from these reactions are the subject of this paper.

#### EXPERIMENTAL CURING

##### *Metallic Lead and Moisture Reactions*

The first approach to acquiring a better understanding of the curing reactions was to trace the changes occurring in several standard production batches of positive plates while they cured. In the early experiments only the two most obvious reactions (oxidation of metallic lead and evaporation of moisture) were followed. Sample plates were taken from the same location in a curing load at various times throughout the cure cycle and each sample

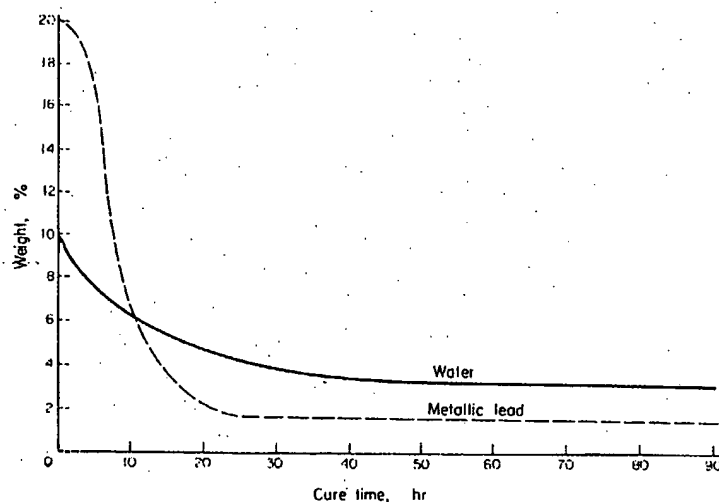


FIG. 1. Metallic lead and moisture content versus cure time.

was analyzed for moisture and metallic lead content. The progress of these two reactions as a function of time in a typical load is illustrated in Fig. 1. The two reactions occur simultaneously and complement each other since water is a necessary catalyst in the exothermic metallic lead oxidation and heat is required to evaporate the moisture from the plate.

To determine the manner in which the metallic lead is distributed and the way in which it reacts, metallurgical specimens were prepared for microscopic examination. Sample plates at various stages of cure were thoroughly dried and impregnated with epoxy resin under a vacuum. Upon hardening, the samples were cross sectioned, ground and polished. The procedures and equipment for sample preparation and microscopic observation were those introduced by Simon<sup>(1)</sup> with only slight modification by the author as previously described.<sup>(2)</sup>

Examination of the mounted, uncured plate segments revealed that the metallic lead particles in plates made with Barton pot type oxide are generally spherical in shape and vary in size from under a micron to about 50 microns in diameter. Partially cured plate segments (Figs. 2 and 3) exhibited particles of lead in an incompletely oxidized state. The centers of the original lead particles remained metallic at this stage while the outer portions have undergone oxidation. As might be expected, very few unreacted metallic lead particles were observed in the fully cured samples.

Another important aspect of the curing reactions—the oxidation or corrosion of the periphery of the grid bars—was not evident in samples



FIG. 2. Partially oxidized particle of metallic lead.

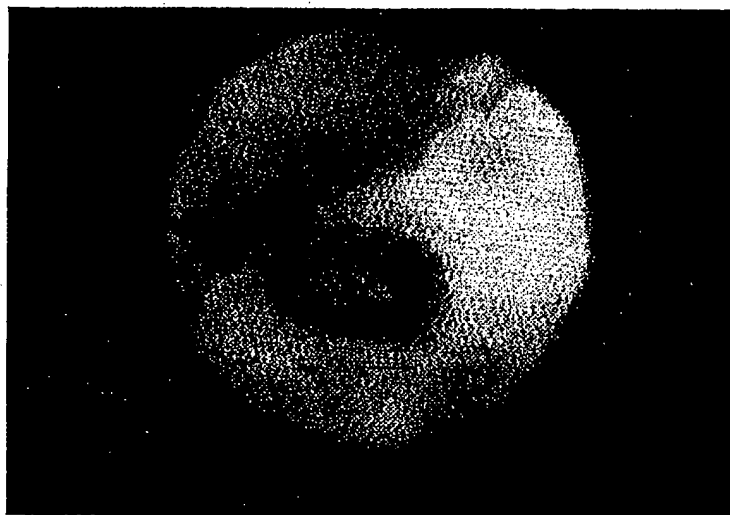


FIG. 3. Partially oxidized particle of metallic lead.

representing the first 24 hr of curing. Apparently the large mass of metal in the grid bar acts as a heat sink and until the entire mass becomes warm, oxidation progress is quite slow. Samples cured for more than 24 hr began to exhibit some grid bar corrosion (Fig. 4). The oxidized ring around the grid

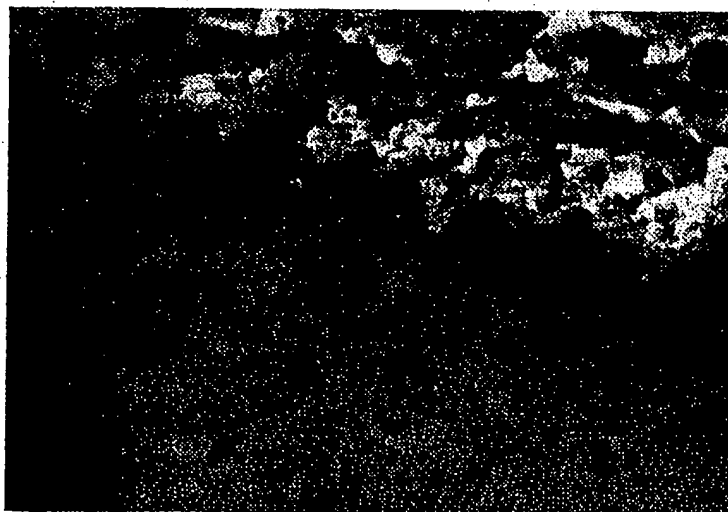


FIG. 4. Oxidation of grid bar periphery during curing.

bars which results from this reaction improves the bond between the grid and the adjacent paste and, hence, strengthens the plate.

#### Basic Lead Sulfate Reaction

The next series of laboratory experiments undertaken was programmed to determine the effect of various curing parameters (temperature and humidity) on the curing reaction rates and on the crystallography of the cured plate.

Freshly pasted, uncured positive plates were placed in a controlled environment chamber and allowed to cure. Sample plates were removed after various cure durations, analyzed, mounted and polished as described above. The temperature within the chamber was varied between 100°F and 200°F and the relative humidity between 20 and 100 per cent.

Plates cured in the lower relative humidity range (<80 per cent) tended to dry out quickly leaving large quantities of unoxidized metallic lead. To avoid this condition, 100 per cent relative humidity was established as a standard for all subsequent curing experiments.

As the cure temperature was increased beyond 100°F, very little improvement in the rate of oxidation was noted; however, a change in at least one physical property—color—was quite obvious. Plates cured at temperatures below about 150°F changed very little in color—retaining their original yellowish-beige color throughout the cure cycle. Plates cured above this temperature, however, turned orange or reddish-orange by the time they were completely cured—the higher temperatures producing the darker colors. The color change could not be attributed directly to the oxidation of lead because virtually all of the metal was oxidized during the curing of the light as well as the dark plates. The color of plates cured at high (180°F) and low (120°F) temperatures as a function of time, measured with a reflectance colorimeter is indicated in Fig. 5. The high temperature curve shows a gradual darkening of the plate beginning at a cure time of approximately 10 hr, followed by an abrupt point of inflection (darkening) after about 20 hr of curing and then a levelling off from a cure time of 24 hr on. X-ray diffraction equipment was used as a supplementary tool to the microscope in determining the crystallographic significance of the high temperature color change.

The X-ray diffraction patterns, as traced by a diffractometer, identified the materials present in the uncured plates as metallic lead, lead monoxide (tetragonal), lead monoxide (orthorhombic), and tribasic lead sulfate hydrate ( $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ ). The low-temperature-cured (light colored) plate contained the same compounds throughout curing, but, of course, the amount of metallic lead present diminished with increasing cure time. Diffraction patterns of the high-temperature-cured positive material began to show peaks for another basic sulfate—tetrabasic lead sulfate ( $4\text{PbO} \cdot \text{PbSO}_4$ )—



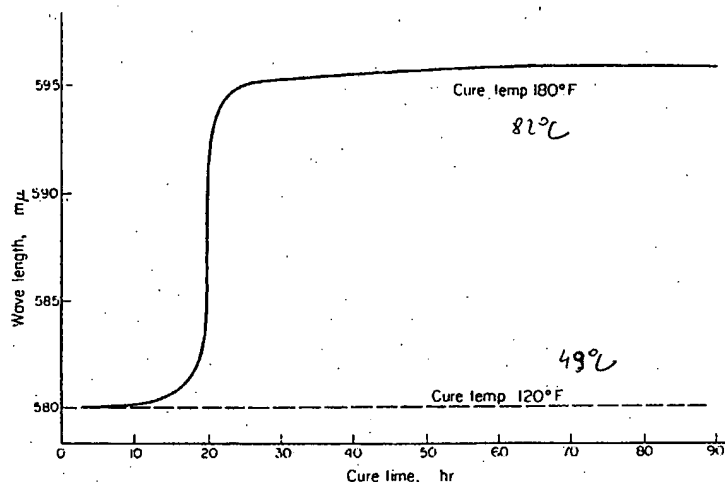


Fig. 5. Colorimetric analysis—positive plate color versus cure time.

after about 10 hr of curing. The change in sulfate form began to occur at the same time as the initial change in plate color was detected. The intensity of the tetrabasic lead sulfate peaks of the high-temperature samples increased with increasing cure time while those for tribasic lead sulfate decreased. The dark reddish-orange plates which were cured for 48 hr at 180°F showed no tribasic lead sulfate—only tetrabasic.

82°C  
An internal standard X-ray diffraction procedure was developed to estimate the quantity of each of the two basic sulfates present in any plate. Using this technique, the high-(180°F) and low-(120°F) temperature-cure processes were followed. Figure 6 is a plot of the quantity of tetrabasic and tribasic lead sulfate versus time for the high-temperature curing process. A similar plot for the low-temperature process would show no tetrabasic lead sulfate and a reasonably constant amount of tribasic lead sulfate with time.

49°C  
The basic sulfate recrystallization was also followed microscopically. Polished samples representing various cure times and temperatures were observed and photographed. In all cases the freshly pasted, uncured positive plates displayed large quantities of metallic lead particles distributed throughout a matrix of light colored, finely divided crystals (Fig. 7). The crystalline matrix was previously identified by X-ray diffraction as lead monoxide and tribasic lead sulfate. With the exception of metallic lead oxidation, little or no change was noted in the structure of the low-temperature-cured plates as they proceeded through the curing cycle. The plate

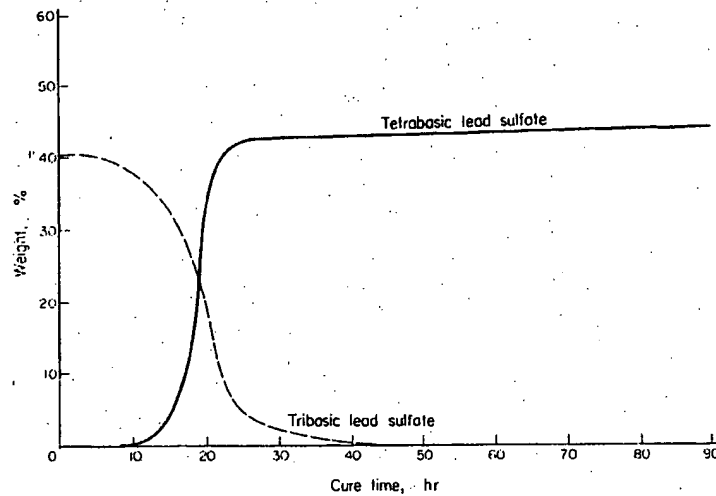


FIG. 6. Basic lead sulfate content versus cure time.

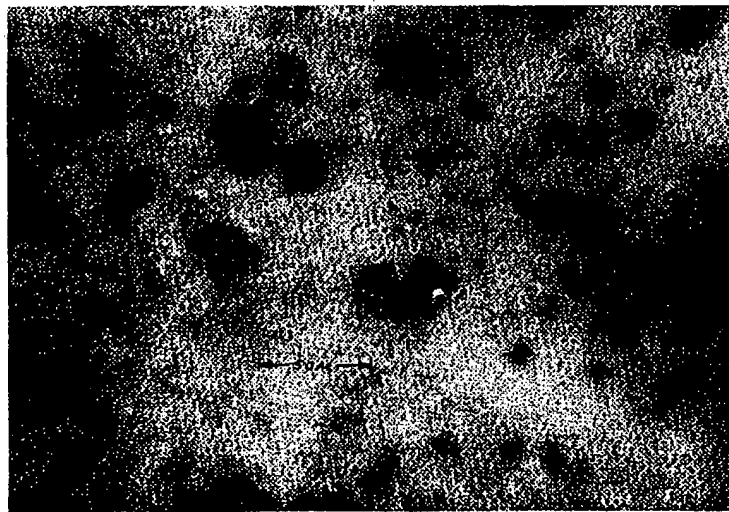


FIG. 7. Microstructure of positive paste—cure time 0 hr. (180°F cure).

specimens taken after 10 hr of high temperature curing (Fig. 8) began to exhibit some large, coarse, dark-colored crystals. After 24 hr of high-temperature curing, the plate was comprised almost exclusively of very

began to  
detected.  
temperature  
basic lead  
cured for  
developed to  
any plate.  
ature-cure  
abasic and  
ig process.  
tetrabasic  
ulfate with  
scopically.  
tures were  
ed positive  
distributed  
g. 7). The  
on as lead  
tallic lead  
v-tempera-  
The plate

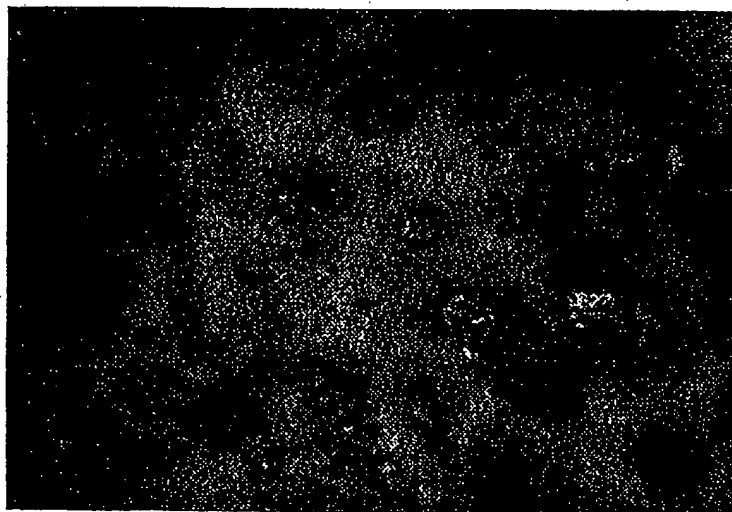


FIG. 8. Microstructure of positive paste—cure time 10 hr (180°F cure).

large, dark orange crystals of material (Fig. 9). These two times (10 hr and 24 hr) correspond to the point at which tetrabasic lead sulfate was first detected and the point where the tetrabasic form became the dominant sulfate in the plate respectively (Fig. 6).

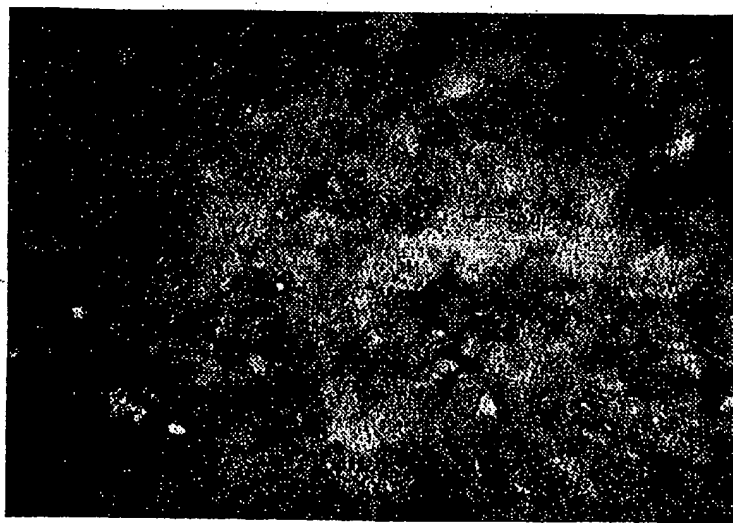


FIG. 9. Microstructure of positive paste—cure time 24 hr (180°F).

## EXPERIMENTAL FORMATION

Several sets of cured positive plates (three to five plates per set) representing the various compositions and crystal structures were electrochemically formed to determine the effect of the two basic sulfates on the electrochemical properties of the plate. The plates to be formed were placed in transparent plastic cells so that the visible formation progress of the positive plates could be observed and photographed. The plates were connected in series and formed at the 20-hr rate (1.6 A) using a constant current, direct current power supply. Standard production negative plates, of identical weight and density, from a single mix were used as the counter electrodes and 1.050 specific gravity sulfuric acid as the electrolyte.

*Photographic Technique*

A 35-mm half-frame camera, mounted on a tripod and equipped with a spring-driven film-advancing motor, was used for photographing the formation progress. A cam-timer was employed to trigger automatically the camera's shutter and photograph the positive plates in the cells each hour during the formation. The timer was programmed for the following sequence: (1) turn the two photoflood lamps on; (2) activate the solenoid which, in turn, pneumatically advances the cable release plunger, thus opening the shutter and taking the photograph; (3) deactivate the solenoid thus pneumatically withdrawing the plunger, advancing the film to the next frame and cocking the shutter for the next picture; and (4) turn the photoflood lamps off. With this automated set-up no attendant was required. High-speed color reversal film was used and the resulting positive slides and color prints were compared in sequence.

*Experimental Formation No. 1*

The three positive plates shown in Fig. 10 originated in a single batch of paste. The light-colored (yellowish-beige) one at the left was cured at 120°F for 48 hr and contains no tetrabasic lead sulfate. The center plate, which is yellowish-orange, was cured at 150°F for 48 hr and is comprised of both tribasic and tetrabasic lead sulfate. The right-hand plate (dark reddish-orange) was cured for 48 hr at 180°F and all of its lead sulfate is in the tetrabasic form—no tribasic lead sulfate was detected in this sample. The curing of all three plates was carried out in a 100 per cent relative humidity atmosphere.

The three plates were formed in individual cells and the progress photographed as described above. Figure 10 shows the three positive plates at the start of formation. In Figure 11 the plates have been formed for 5 hr and the originally dark-colored, right-hand plate exhibits more darkened area ( $PbO_2$ ) than either of the other plates. This trend became even more

10 hr and  
was first  
dominant



FIG. 10. Formation of positive plates of varying cure history—formation time 0 hr.

48°C/2d

66°C/2d

82°C/2d

100% relative  
humidity

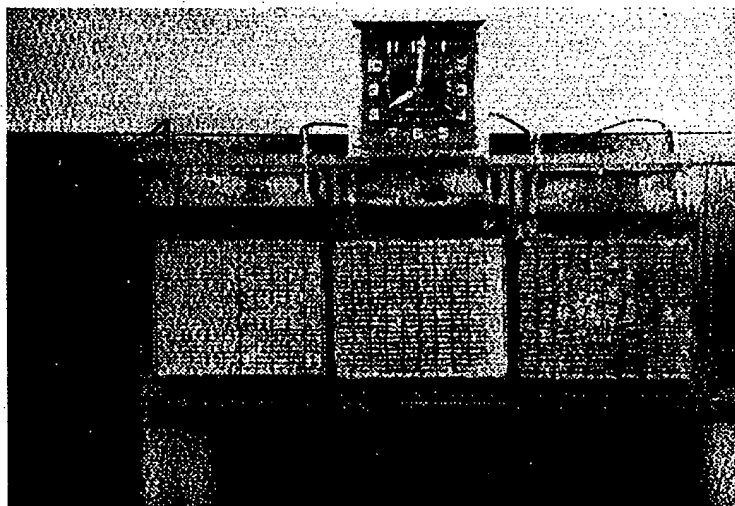


FIG. 11. Formation of positive plates of varying cure history—formation time 5 hr.

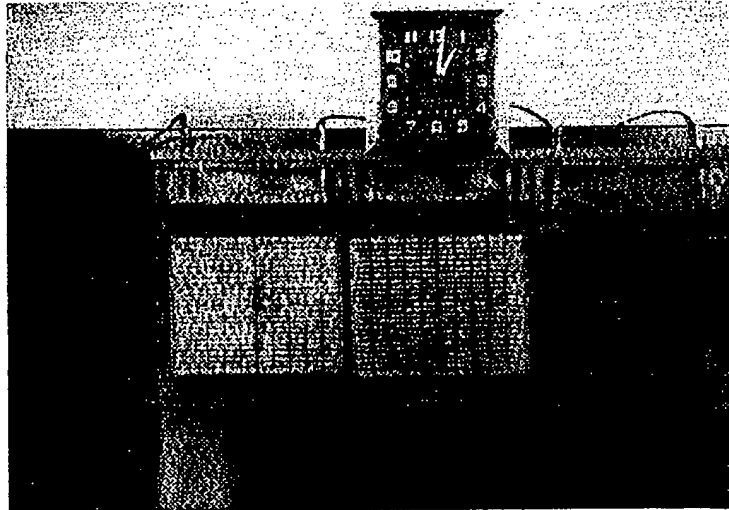


FIG. 12. Formation of positive plates of varying cure history—formation time 10 hr.



FIG. 13. Formation of positive plates of varying cure history—formation time 15 hr.

noticeable in subsequent photographs. After 10 hr of formation (Fig. 12) one-half of the total number of ampere hours has been put into the plates. Here the plate at the right, which contained tetrabasic lead sulfate before formation, was apparently nearing the completion of formation while the other two plates were in a relatively unformed state. In Fig. 13 the plates have undergone 15 hr of formation and the high-temperature-cured plate at the right appears to be completely formed, while the formation of the

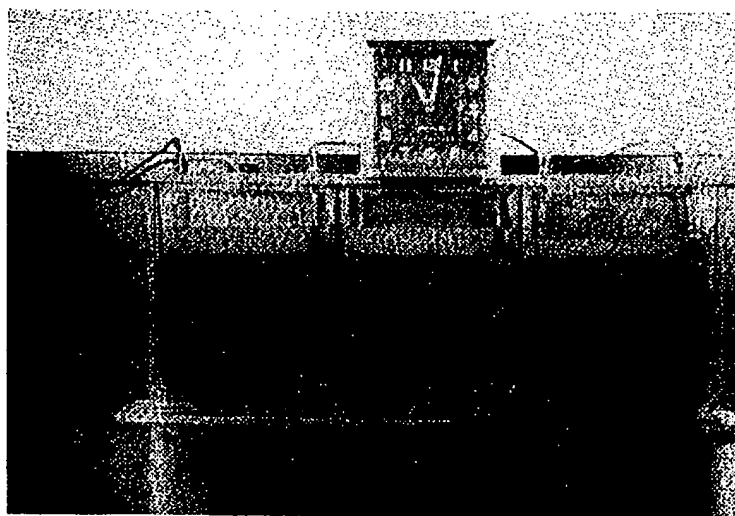


FIG. 14. Formation of positive plates of varying cure history—formation time 20 hr.

other two plates continues. Figure 14 shows the three plates as they completed the twentieth and final hour of formation. In this photograph it appears that the formation of all three plates has been completed.

After 20 hr of formation, the current was turned off and the plates were washed and dried. The active material from each plate was analyzed for the total amount of lead dioxide present by wet chemistry methods and for the ratio of alpha to beta dioxide by X-ray diffraction. A slightly modified version of the Dodson<sup>(3)</sup> technique was used for the polymorphic ratio determination. Segments of each of the three formed positive plates were mounted and polished for microscopic examination as described above. The results of the determinations are as given in Table 1.

The results are reported as the weight per cent lead dioxide and the portion, by weight, of the  $\text{PbO}_2$  which appears as the alpha polymorph.

Fig. 12)  
e plates.  
e before  
hile the  
ie plates  
ed plate  
n of the

The subsequent microscopic examination of the metallurgically prepared samples served to confirm the analytical results and to characterize more completely the crystallographic nature of the formed positive active material.

TABLE 1. FORMED POSITIVE PLATE COMPOSITION  
EXP. FORMATION NO. 1

	Plate No.	Unformed color	% PbO <sub>2</sub>	% $\alpha$ -PbO <sub>2</sub>
42°	1 (left)	Yellowish-beige	80.0	23.0
60°	2 (center)	Yellowish-orange	71.5	28.7
82°	3 (right)	Reddish-orange	52.4	36.4

The formed sample representing the originally light-colored positive plate appeared to be almost completely converted to finely divided lead dioxide and a good share of the lead dioxide was of a reddish-brown color indicating a preponderance of beta lead dioxide.

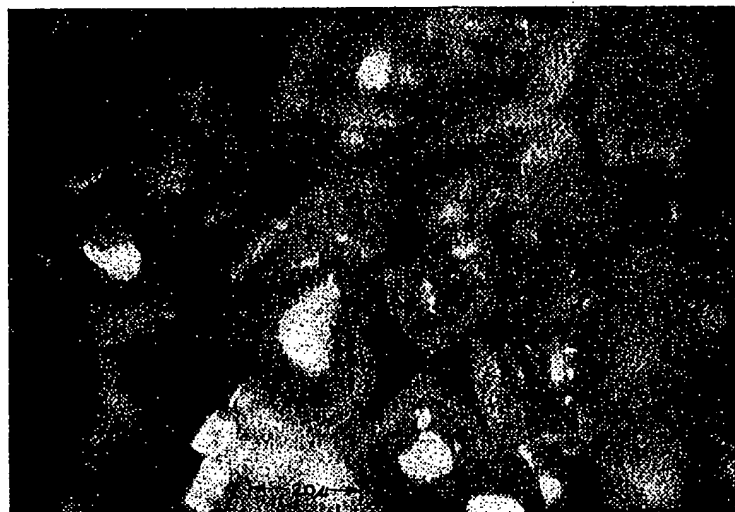


FIG. 15. Microstructure of high-temperature cured positive paste after formation.

Examination of the formed positive material originating from the dark reddish-orange unformed plate revealed quite a different structure. The majority of the coarse crystals which made up this specimen appeared to be incompletely formed. The peripheries of the large tetrabasic lead sulfate crystals were converted quickly to lead dioxide giving the outward appear-

ey com-  
graph it  
l.

tes were  
yzed for  
ods and  
ly modi-  
hic ratio  
tes were  
ve. The

and the  
morph.



ance of early and complete formation, but the centers of these crystals remained as unconverted sulfate even after 20 hr of formation (Fig. 15). Much of the lead dioxide present in this sample was of the dark greyish-black color which is characteristic of the alpha polymorph.

#### *Experimental Formation No. 2*

A set of five identical plates, all of which were cured at 180°F, was connected in series and formed at the 20 hr rate. One of the cells was disconnected from the circuit after 5 hr of formation, another after 10 hr, a third after 15 hr and a fourth after 20 hr. The remaining plate was allowed to complete the scheduled 20 hr of formation plus an additional 5 hr, for a total of 25 hr. The plates were washed, dried and analyzed for alpha and beta lead dioxide and total lead dioxide. Segments of each plate were mounted and polished for microscopic examination. The analytical results obtained are given in Table 2.

TABLE 2. POSITIVE PLATE COMPOSITION  
EXP. FORMATION NO. 2

Plate No.	Hours of formation at 20-hour rate	% PbO <sub>2</sub>	% α-PbO <sub>2</sub>
1	5	37.2	39.2
2	10	45.5	37.7
3	15	53.7	36.8
4	20	54.3	36.2
5	25	53.6	37.5

The majority of the conversion from divalent lead compounds to lead dioxide in these plates occurred within the first 5 hr of formation. By the end of the fifteenth hour of formation, the progress ceases and no further conversion takes place. This time (fifteenth hour) coincides with the point at which the high-temperature-cured plate in the previous experiment gave the outward appearance of being completely formed. It is also quite obvious from the data that the additional 5 hr of formation time did not improve the degree of completion of the formation reactions.

The proportion of the lead dioxide which occurred as the alpha polymorph (%α-PbO<sub>2</sub>) remained quite constant with increasing formation time.

#### CONCLUSIONS

The temperature attained during curing markedly affects the crystal structure and composition of the formed as well as the cured positive lead-acid battery plate.

When a positive plate undergoes high-temperature curing ( $>150^{\circ}\text{F}$ ), the finely divided crystals of tribasic lead sulfate present recrystallize as large, coarse crystals of tetrabasic lead sulfate. This recrystallization is generally accompanied by a change in plate color from a yellowish-beige to a dark reddish-orange.

Plates which contain a significant quantity of the large tetrabasic lead sulfate crystals appear to convert very rapidly to lead dioxide on formation. Actually the electrochemical conversion to lead dioxide is only superficial since the formation does not penetrate into the centers of the crystals. The ramifications of this type of incomplete formation should be quite apparent to those familiar with battery manufacturing and testing.

First, since only slightly more than half of the material (52.4 per cent) in the high-temperature-cured plates is actually converted to useable lead dioxide and a large portion of that (36.5 per cent) is in the lower capacity  $\alpha\text{-PbO}_2$  form, initial yields or efficiencies for a battery containing this type of plate would be extremely low.

Secondly, on subsequent cycling, more of the interior of these crystals would be converted to lead dioxide thereby releasing additional sulfate ions. This would lead to high electrolyte specific gravity and uneven gravities or concentrations from one cell to the next.

Both of the above effects were verified by assembling and testing batteries containing plates cured at elevated temperatures.

Tetrabasic lead sulfate crystals and the lead dioxide crystals which they are converted to during formation *do* have some desirable characteristics. The surface of these crystals forms very rapidly and serves to distribute the formation current throughout the plate. The size and high density of the crystals also would appear to enhance the mechanical strength of the material. If recrystallization of the basic sulfates can be regulated such that the quantity, shape and distribution of these crystals is optimized, it should be possible greatly to improve the efficiency and strength of the positive active material during formation and subsequent cycling.

Another approach designed to take full advantage of the crystallographic transformation would be aimed at methods for more completely converting the centers of the crystals to lead dioxide—preferably the higher capacity beta polymorph. This would result in a cellular structure with a hard, dense, conductive outer layer surrounding a high-capacity, finely divided central portion. This type of structure, if obtainable, would closely resemble that which Simon<sup>(4)</sup> noted and Burbank<sup>(5)</sup> characterized in examining long-lived positive lead-acid submarine battery plates.

The original photographs were in color and some of the contrast and resolution has naturally been lost in conversion to black and white prints for publication.

## REFERENCES

1. SIMON, A. C. *Electrochem. Tech.* **1**, 82 (1963).
2. PIERSON, J. R. *Electrochem. Tech.* **5**, 323 (1967).
3. DODSON, V. H. *J. Electrochem. Soc.* **108**, 401 (1961).
4. SIMON, A. C. *Batteries 2, Research and Development in Non-Mechanical Electrical Power Sources*, COLLINS, D. H. (Ed.), Pergamon, London and New York (1965).
5. BURBANK, J. *Batteries, Research and Development in Non-Mechanical Electrical Power Sources*, COLLINS, D. H. (Ed.), MacMillan, New York (1963).

## DISCUSSION

G. C. CROW (*Joseph Lucas (Batteries) Ltd.*): Do you attribute the very large tetrabasic lead sulfate crystals produced, and the fact that they were difficult to anodize, to the fact that you were using Barton pot oxide which has comparatively large dense particles?

J. R. PIERSON: I do not know that I can attribute it to the type of oxide used, perhaps you would not get the same size crystals and the difficulty in anodizing the crystals if you used ball mill oxide. We are in the business of manufacturing the oxide by the Barton process and most of our experiments for that reason were with Barton type oxides. We have run a few experiments with ball mill oxide but not enough to make a comment on it.

G. C. CROW: Were you able to positively identify the substance remaining unformed in the centre of the tetrabasic crystals, and, if so, was it sulfate, or some form of  $PbO$ , or both?

J. R. PIERSON: We obtained X-ray diffraction patterns when we saw these incompletely formed crystals, and surprisingly enough the interior of the crystals was basic lead sulfate. Apparently because of the inability of the electrolyte (sulfuric acid) to penetrate the periphery that has been previously formed to lead dioxide, further sulfation of the interior does not occur. Therefore the interior still seems to be in the tetrabasic lead sulfate form.

G. UFFENBROEK (*Oldham & Son Ltd.*): Are you aware of the literature in which it is suggested that the oxidation of lead during the curing process might temporarily give rise to the existence of hydrogen peroxide within the cured mass and would this, in your view, alter the reaction mechanism which has been proposed by some speakers at this meeting and which perhaps you may have in mind?

J. R. PIERSON: I have been unable to detect any hydrogen peroxide in material undergoing curing. I don't think I am familiar with the paper that you are referring to.

QUESTIONER: It can be found in Mellors Modern Inorganic Chemistry under the section of lead, where it deals with oxidation of lead.

T. R. CROMPTON (*Oldham & Son Ltd.*): In your curing experiments were the plates packed tightly together or racked separately, and would you expect your conclusions to be altered depending on these two extremes?

Its very pleasing to see that an X-ray method now appears to be in almost routine use for distinguishing two forms of lead sulfate, I was wondering whether this work had been published or whether you are intending to publish it.

J. R. PIERSON: It is an internal standard X-ray diffraction technique which we developed but have not published, I have not any plans to publish it. If you look down towards the low angle end of the X-ray diffraction trace of the tribasic and tetrabasic lead sulfates, I think you will find the two peaks that are most easily distinguished as being characteristic; one of tribasic lead sulfate and the other of tetrabasic lead sulfate. It is then a relatively simple matter to build in an internal standard peak in this general area and compare each of the sulfate peaks to it. You are then (within 10 or 15%) reasonably sure of what your composition is at any time.

In our early studies, we stacked the plates in a manner similar to that used in the early studies at Lucas. Then we stacked the plates individually. Most of our experiments were on very small batches, half a dozen to ten plates perhaps, and they were usually racked to obtain reasonably uniform conditions for each of the plates. I think it would probably make a difference if they were stacked very high.

S. C. BARNES (*Joseph Lucas (Batteries) Ltd.*): In the X-ray diffraction analysis showing the conversion of the tribasic sulfates to tetrabasic sulfate, did you observe whether it was

the orthorhombic or the tetragonal oxide which was preferentially "absorbed" into the tribasic sulfate. This would help resolve a perennial question which is raised among battery people. The orthorhombic is less reactive than the tetragonal form.

J. R. PIERSON: This, perhaps, is one of the things that prompted Mr. Crow's question on a very convenient way to determine the answer to your question. It would be very simple to make a high orthorhombic lead oxide with the Barton system and compare it with a tetragonal oxide from the ball mill system. The question has arisen in my mind but I haven't resolved it yet.

J. P. G. FARR (*Metallurgy Dept. University of Birmingham*): In connection with the question by Dr. S. C. Barnes concerning the production of  $\text{PbO}_2$  from tetrabasic sulfate during formation, observations made by G. W. Greene and myself on the corrosion of the positive plate during service may be relevant. In a thin corrosion layer adjacent to the grid are found basic sulfate (in particular  $4\text{PbO} \cdot \text{PbSO}_4$ ) and retained antimony. This suggests corrosion under conditions of reduced acidity (cf. curing). In a thicker, outer corrosion layer is found  $\text{PbO}_2$  (90%  $\alpha$ , 10%  $\beta$ ). Antimony is removed from the initial layer in its transformation to the second layer. The latter thickens during service life, suggesting that it is comparatively unreactive electrochemically. If this thicker layer were converted to  $\text{PbSO}_4$  on discharging then, following Burbank (*J. Electrochem. Soc.* **106** (1959), 369) and Bagshaw and Wilson (*Electrochem. Acta* **10** (1965), 867), one would expect  $\beta\text{PbO}_2$  to be formed on recharging. The initial corrosion layer is up to  $10\mu$  in depth. It was characterized by electron diffraction using an A.E.I. EM6 electron microscope modified to give an expanded camera constant. This technique, which allowed basic sulfates to be distinguished, is to be published (B. Duggan and G. W. Greene, *J. Roy. Microscopical Soc.*, 1968).

## THE ELECTROCHEMICAL SOCIETY SERIES

THE CORROSION HANDBOOK  
*Edited by Herbert H. Uhlig*

MODERN ELECTROPLATING, THIRD EDITION  
*Edited by Frederick A. Lowenheim*

THE ELECTRON MICROSCOPE  
*Edited by T. D. McKinley, K. F. J. Heinrich and D. B. Wittry*

CHEMICAL PHYSICS OF IONIC SOLUTIONS  
*Edited by B. E. Conway and R. G. Barradas*

HIGH-TEMPERATURE MATERIALS AND TECHNOLOGY  
*Edited by Ivor E. Campbell and Edwin M. Sherwood*

ALKALINE STORAGE BATTERIES  
*S. Uno Falk and Alvin J. Salkind*

THE PRIMARY BATTERY (*in Two Volumes*)  
*Volume I Edited by George W. Heise and N. Corey Cahoon*  
*Volume II Edited by N. Corey Cahoon and George W. Heise*

ZINC-SILVER OXIDE BATTERIES  
*Edited by Arthur Fleischer and J. J. Lander*

LEAD-ACID BATTERIES  
*Hans Bode*

*Translated by R. J. Brodd and Karl V. Kordesch*

## THE CORROSION MONOGRAPH SERIES

*2. T. Foley, N. Hackerman, C. V. King, F. L. LaQue, H. H. Uhlig, Editors*

THE STRESS CORROSION OF METALS, *by Logan*  
CORROSION OF LIGHT METALS  
*by Godard, Bothwell, Kane, and Jepson*

THE CORROSION OF COPPER, TIN, AND THEIR ALLOYS  
*by Leidheiser*

CORROSION IN NUCLEAR APPLICATIONS, *by Warren C. Berry*  
HANDBOOK ON CORROSION TESTING AND EVALUATION,  
*Edited by William H. Ailor*

## LEAD-ACID BATTERIES

HANS BODE

RESEARCH DIRECTOR (RETIRED)  
VARTA BATTERIES AG  
HANOVER, GERMANY

*Translated by*

R. J. BRODD and KARL V. KORDESCH

UNION CARBIDE CORPORATION  
CLEVELAND, OHIO

*Sponsored by*

THE ELECTROCHEMICAL SOCIETY, INC.  
Princeton, New Jersey

A WILEY-INTERSCIENCE PUBLICATION

JOHN WILEY & SONS

NEW YORK • LONDON • SYDNEY • TORONTO

The internal surface is dependent on the particle-size distribution, on the particle shape and on the oxide content.

### 3.3 PASTE PREPARATION AND CURING PROCESSES

In this section the relation between the characteristics of the lead dusts, the paste preparation, and the curing process are treated. Their relation to the electrical properties of the plates are discussed in Section 3.4.

To prepare a *formable* plate from lead dust a *pasteable* mass is prepared from air-dried powder with water and sulfuric acid applied to the active mass carrier (grid), and subsequently cured (see Section 2.6). In the dried plate the material must possess a certain dry strength so that it cannot fall out in the subsequent manufacturing procedures which, depending on formation, may differ.

Other characteristics that are important after conversion of the dusts and pastes into porous electrodes include the following

1. Porosity (overall value).
2. Pore distribution and average pore diameter.

In order to follow the preparation of plates from dust: it is assumed that a mixture (a heterogeneous multiple-phase system comprised additively of all components  $1, \dots, i, \dots, l$ ) is present in all stages. Among the individual materials  $M_i^*$  of component  $i$ , the mole number  $n_i$  is obtained by dividing by the molecular weight  $M_i$ ,  $n_i = M_i^*/M_i$ . For lead dust with the oxide weight fraction  $w_2$  we obtain the number  $n_i$  of moles of metallic lead  $n_1 = (1 - w_2)/207.19$  and  $n_2$  of  $PbO$ ,  $n_2 = w_2/223.19$ . If more components are added, an analogous calculation for every component applies.

If the sulfuric acid is converted to tribasic sulfate and the portion  $\Delta n_1$  of the metallic lead is oxidized, the system consists of

$$\begin{aligned} & (n_1 - \Delta n_1) \text{ moles of lead} \\ & (n_2 - 4n_3 + \Delta n_1) \text{ moles of lead oxide} \\ & n_3 \text{ moles of tribasic sulfate} \\ & n_4 \text{ moles of water} \end{aligned}$$

If tetrabasic salt is formed, we find  $(n_2 - 5n_3 + \Delta n_1)$  moles of oxide,  $n_3$  moles of tetrabasic sulfate, and  $(n_4 + n_3)$  moles of water.

These numbers permit the calculation of a series of properties of the paste or the system:

1. The total material from the molecular weights.
2. The total volumes from the molar volumes.
3. The density for (1) to (2).

4. The total heat capacities from the molar heat capacities
5. The specific heat from (1) and (4).

Likewise, the contribution of the individual components to the total volume, the total heat capacity, and so on, can be found.

If the material contains  $n_1$  mole of metallic lead and  $n_2$  moles of lead compounds, the theoretical Ah capacity is given by  $2F(n_1 + n_2)$  or  $(n_1 + n_2)(53.6)$  Ah. Dividing by total mass or volume, we obtain the specific capacity. The molar values of components of active materials in the lead storage battery are listed in Table 2.4.

### MANUFACTURING PROCEDURES

As in all manufacturing procedures, we can distinguish discontinuous and continuous processes in which, in the trend of automation, continuous processes become significant when combined with proper control procedures.

The discontinuously operating mixing and kneading machines (capacity between 300 and 1200 kg of powder) have a mix-feed container of cast iron or acid-resistant steel. The blades for working the material may operate horizontally or vertically. The removal of the finished mass is accomplished by tilting the container or by opening the bottom.

The paste consistency depends on the manner of loading the mixer. If the dust is loaded first, water and acid may be added in various ways (Table 3.3).

In all cases the same paste density is attained, aside from water loss by vaporization, but consistency and plasticity may vary over a wide range. For the same mixing ratios (the same total amounts of water and sulfuric acid) the dust is treated with dilute acid before the remaining water is added. This procedure produces masses with the best plastic properties. If a concentrated acid is added first, hard grainy mixtures form. The lead sulfate formed because of localized enrichment in sulfuric acid converts with difficulty to basic lead sulfate in the brief mixing period. The paste should have a crisp, crumbly consistency, not creamy, sticky, or salvelike.

The relationships are similar if the loading of the mixer starts with water and sulfuric acid. Dust may be added to the most dilute acid, more uniform and better plastic masses are produced if only part of the water is mixed with the powder and the acid is added as the last component. The acid concentration is carefully selected so that the required amount is attained. Fibers (mostly dyne) are added for positive plates during the production process for the purpose of increasing their strength and reducing mud formation.

Some additives are required for negative plates. A dry premix is prepared with part of the dust and additive which is fed in suspension to the rest of

the mix in the mixer. The additive may also be added dry to an otherwise finished paste.

Heat evolution occurs during the mixing process from mechanical friction and chemical reaction. Generally, cooling is necessary. The temperature of the paste should not exceed 65 to 70°C (see Sections 2.1 and 3.3 and Pierson, 1970). The mass loses too much water above this temperature so that paste density, paste workability, theoretical capacity, and porosity are influenced unfavorably.

Cooling can be done with coils or jackets. In cooling by blowing air, heat is removed by the evaporation of water from the paste but additional heat is produced simultaneously because of the intensified oxidation. In the batch process a certain amount of cooling occurs during the unloading and during cleaning of the machine.

The mixer also kneads the active masses. For all machines in use a completely uniform distribution of the components is attained in about 15 to 30 minutes.

For continuously operating machines the same principles apply. Good heat transfer must be provided, for the closed structure prevents cooling by evaporation and during unloading. Because the evaporation of water is suppressed, more uniform pastes can be expected. Scales and metering devices are required for the loading and discharging of the mixers, manually or automatically, on a predetermined schedule. Temperature control is essential. Control of manufacturing occurs mainly by measuring the paste density (cube density), which provides control of the prescribed water content of the paste for a similar dust and constant sulfuric acid content.

The paste density must be controlled, for it determines the theoretical input and useful capacity through the porosity of the plates. Whatever paste density must be maintained, it depends primarily on the dust and mixing instructions and the type of pasting machine.

The finished pastes are fed to pasting machines in which the grids are automatically loaded or "pasted." Pasting by hand is done only in special cases. The pasting machines have a station for grid loading, a device for separating the grids, which are loaded in stacks, transfer devices for grids and masses, a mass container with the pasting devices, and a dimensional control device for the plate thickness, and a conveyor line for the pasted, still wet plates.

The following machine designs can be differentiated:

1. The position of the grid under the pasting tool; lengthwise, crosswise, or round table pasting machines.
2. The spatial position of the grid; horizontal or vertical pasting machines.

"All pastes contain 62 g H <sub>2</sub> SO <sub>4</sub> ."																	
Paste No.	Water: Amount, cm <sup>3</sup>	Time, min	Acid: Density, kg/liter	Amount, cm <sup>3</sup>	Time, min	Water: Amount, cm <sup>3</sup>	Time, min	Mixing Time, min	Temperature (maximum), °C	Total heat, kJ	Frictional heat	Chemical heat	Heat of dilution	Reaction heat	Paste density, kg/liter	Quality of paste	
1	—	—	—	244	23.5	—	—	35	46.5	111.5	109.0	73.5	29.0	0	29.0	3.60	Very good
2	115	2.8	1.283	130	4.7	—	—	30	52	50	124.0	86.5	37.5	3.0	32.5	3.54	Good
3	60	1.0	1.283	130	4.7	55	1.0	35	58	58	112.0	72.0	40.0	3.0	37.0	3.57	Good
4	—	—	—	130	4.7	115	2.5	30	30	47	113.0	61.5	51.5	10.5	41.0	3.47	Sandy
5	173	2.2	1.473	73.8	2.3	—	—	30	30	53	129.0	73.5	67.0	55.5	10.5	45.0	Good
6	60	1.0	1.473	73.8	2.3	113.1	1.0	30	30	53	129.0	73.5	67.0	55.5	10.5	45.0	Sandy
7	—	—	—	1.473	73.8	2.3	173	1.2	30	63	128.0	61.0	10.5	50.5	3.60	Dead, sandy	

3. The number and arrangement of pasting tools: one-sided or two-sided pasting machines.
4. The method of feeding the active mass: machines with blades and disks or rolls.
5. The method of transporting the grids: machines with conveyor, chains, or rolls or with templates to pick up the grid.

The machines can be equipped for calibration of the unpasted grid with stationary or rotating cutting tools. After pasting the material into the grid, the plates move to a rolling mill with adjustable separation for smoothing the two surfaces with stripping plates or other sizing devices.

For machines operating from both sides the material is pressed harder so that the mass loses water and the surface becomes smoother and denser than the interior. This process makes it more difficult to obtain uniform and crackfree shrinkage and the oxidation of metallic lead during the subsequent curing process. Pasting machines operating on one side press to a nearly constant water content and achieve more uniform porosity. This facilitates the "ideal" shrinkage process required for crackfree drying and the oxidation of lead.

The curing process consists of the conversion of wet pasted plates to a dry, crackfree, unfurnished plate of sufficient strength (dry strength) and adhesion to the grid. During this process two steps proceed simultaneously and in sequence (see Section 2.6):

1. Water loss by shrinkage.
2. Void formation.

Curing is an important part of manufacturing, for if it is not properly carried out capacity and especially life expectancy are adversely influenced. The curing can be done in different ways.

1. The plates are suspended individually on racks with small separations. According to a pre-established program, the plates are subjected to a flow of damp or dry air and finally heated. The curing and drying lasts about 16 to 24 hours.
2. The plates are hung on chains and moved through a tunnel kiln in which temperature is increased and humidity is decreased. The kiln is usually heated with  $\text{CO}_2$ -containing combustion gas which passes through the kiln.
3. The plates are flash-dried by gas heating or infrared heating so that they may be packed densely 20 to 30 cm high without sticking. They are covered

to prevent the process from proceeding too rapidly. Otherwise small cracks will appear. For oxidation and drying in stacks 4 to 6 days are required.

4. The plates are dipped in sulfuric acid or sprayed with sulfuric acid to form a dense lead sulfate film on the surface (pickling), a process frequently used for tubular plates (see Section 3.4) but less often for grid plates. For grid plates the formation of cracks on drying is retarded by treatment with dilute sulfuric acid. The related curing and drying is then carried out by procedure 1 or 3.

After curing the paste in the plates must have sufficient dry strength and adequate adhesion to the grid so that it does not detach during subsequent manufacturing steps and retains electrical contact with the grid during formation.

The plates obtained by proper curing can be handled without creating problems in the subsequent processing steps, are almost entirely free of metallic lead, and can be stored indefinitely in this state. In principle, damp plates may be formed immediately.

#### CHEMICAL PROCESSES

Lead dust mixed with water reaches a slightly alkaline pH value of about 9. Mill dust contains tetragonal  $\text{PbO}$  exclusively, whereas thermal dusts also contain rhombic  $\text{PbO}$  (up to 10% by weight). Occasionally some minium is found, sometimes added intentionally. Rhombic  $\text{PbO}$ , as the unstable modification, reacts preferably with sulfuric acid.

The amount of sulfuric acid added during mixing is not large enough to form neutral or monobasic sulfate. These two substances can form only when rapid addition, without sufficient stirring, causes localized high concentrations of sulfuric acid. Slower addition and vigorous mixing produce only higher basic sulfates. In the pH range in which the paste is in equilibrium with lead oxide only tribasic and tetrabasic sulfate form. Here temperature and amount of acid are significant.

At low temperatures and with the usual amount of acid tribasic sulfate results. It should decompose at  $100^\circ\text{C}$  but absorbs additional  $\text{PbO}$  and releases water above  $70^\circ\text{C}$  whenever the temperature in the paste rises sufficiently over long periods. This process occurs not only during mixing but also on curing in drying ovens and perhaps even during formation. Active materials with appreciable portions of tetrabasic sulfate are difficult to form according to Ikari et al. (1959) and Pierson (1970) and tend to form sludge. The mixing and curing processes must be carried out so that only tribasic sulfate will form (see Figure 3.6).





Figure 3.6 Electron microscope picture of the surface of a pasted plate *before* curing, enlargement 1:23,200 (Courtesy of ESB Inc.).

Lead paste always contains unchanged oxide, for the metallic lead is slowly oxidized during all mixing and curing processes. Also white hydrate and rhombic oxide can form (see Section 2.1). At the completion of the curing process the Pb must be oxidized until the residue is smaller than 5%. A Pb content of more than 5% is supposed to cause difficulties during the formation of positive plates (swelling or warping or extensive sludge formation).

During the initial stages of the formation of sulfate the components are often not identifiable by X-rays. At first crystal seeds are produced in sizes smaller than 10 nm which are X-ray amorphous. The strongly characteristic X-ray lines of tribasic sulfate appear later after recrystallization, a process (ripening) that continues in tribasic sulfate during curing until the crystallites can be seen optically and the submicroscopic and colloidal particles have almost disappeared. On conclusion of the process needleshaped crystals

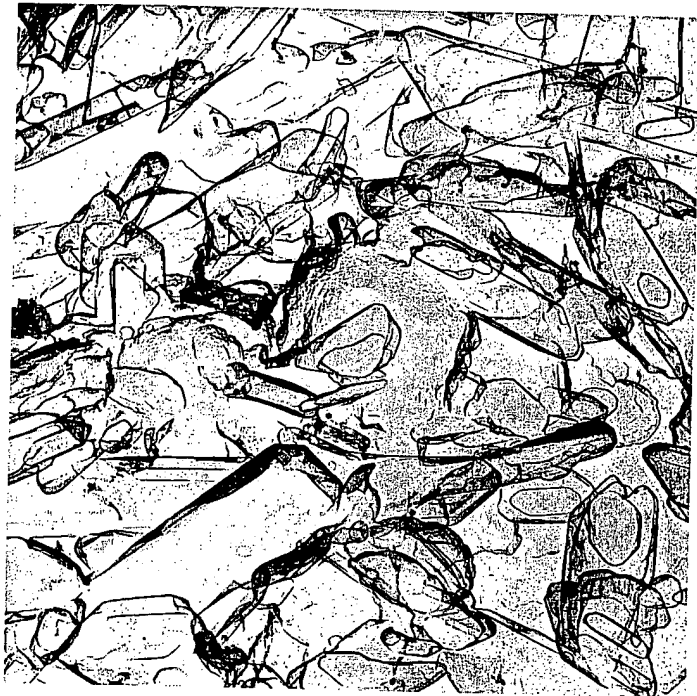


Figure 3.7 Electron microscope picture of the surface of a pasted plate *after* curing, enlargement 1:23,200 (courtesy of ESB Inc.).

of 1  $\mu\text{m}$  in thickness and several  $\mu\text{m}$  in length may be found [see Figures 3.6 to 3.8, Mrgudich (1942); Sections 2.6 and 2.7].

After the mixing process a paste contains the following solid components: unchanged (tetragonal) and freshly formed (rhombic) lead oxide, tribasic sulfate as the component containing the added sulfuric acid, and finally some metallic lead the amount of which is decreased in comparison to the starting value. Added minimum is not changed by mixing, for the process proceeds in an alkaline medium unless localized overacidification occurs. After curing the crystals are generally better formed and the metallic lead is oxidized to a small "residual lead content."

The formation of basic lead carbonate occurs as a side reaction. It is not detectable in the mass before pasting. On the other hand, the surfaces of the pasted plates contain larger amounts of carbonate. During absorption of

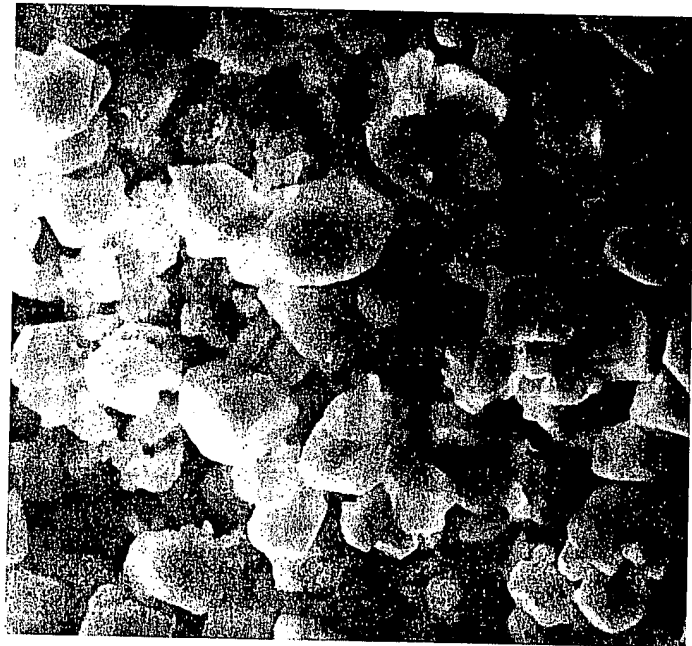


Figure 3.8 Stereo scan picture of the surface of an unformed negative plate; enlargement 1:4600 (G. Sterr, 1970).

$\text{CO}_2$  water is also bonded because basic lead carbonate,  $\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$ , causes the plate surfaces to dry rapidly, thus facilitating their stacking without sticking. Carbonate impedes formation, however. A small carbonate content may still be determined in the plates after many cycles.

#### HEAT EFFECT IN THE MANUFACTURE OF MIXTURES

The temperature in the mixing process affects the composition in the mixture. The undesirable formation of tetrabasic lead sulfate begins above  $70^\circ\text{C}$ . An increase in temperature can occur as a result of enthalpy changes in the chemical reactions as well as frictional heat [see Gillibrand and Wilde (1964)].

The assumptions for the calculation of a maximum temperature contain several factors, in particular, production variables that can only be approximate. For this reason several simplifications that do not substantially affect

#### PASTE PREPARATION AND CURING PROCESSES

TABLE 3.4. ENTHALPY OF NEUTRALIZATION OF  $\text{PbO}$  WITH  $\text{H}_2\text{SO}_4$ <sup>a</sup>

Molality $m_2$ (mole/kg)	100 $w_2$ Mass (%)	Density $\rho$ (kg/liter)	Neutralization Enthalpy $\Delta H_N$ (kJ/mole)
11.101	52.20	1.411	-133.96
5.551	35.20	1.258	-117.01
3.700	26.62	1.183	-113.13
2.221	17.82	1.113	-103.77
1.110	9.82	1.063	-101.32
0.50	4.85	1.029	-100.32

<sup>a</sup> See assumptions in the text.

the results are introduced in the chemical reactions. There are three principal chemical reactions: oxidation of metallic lead; neutralization of lead oxide with sulfuric acid; and formation of hydroxides or hydrates.

The enthalpy change for oxidation of lead under standard conditions may be found in Tables IV to VI in the Appendix.

$$\Delta H_B^\circ = -219 \text{ kJ/mole or } -982 \text{ kJ/kg lead oxide}$$

This value, with the opposite sign, the heat of reaction, is exact only if tetragonal oxide forms. When unstable rhombic modification forms, the somewhat smaller value of  $-217.3 \text{ kJ/mole}$  applies. This difference is neglected in the following. Among the possible neutralization reactions, only the formation of neutral lead sulfate, which includes the assumption that the enthalpies of formation of the basic sulfate are additively composed from its components, is considered. The enthalpy of neutralization depends on the concentration  $m_2$  of sulfuric acid. The values are listed in Table 3.4.

The enthalpy of neutralization is eliminated entirely or in part if presulfated oxide is used (see Section 3.2).

Even when pure water is added to lead dust, there is always a small heating effect. In this case it is not the formation of hydroxides; it apparently arises from the heat of wetting which is not known for the system, lead oxide/water. The amount can be neglected if the surface areas are of the order of magnitude of several  $\text{m}^2/\text{g}$  and the heat of wetting is at  $4 \text{ kJ/kg}$  as in other materials with analogous specific internal surfaces [see Gregg (1958)].

The change in enthalpy may be estimated under simplifying assumptions; for example, when  $\Delta n_1$  mole of lead is oxidized,  $n_3$  mole of lead sulfate is formed. The heat capacity can be calculated (see Table 3.5) from the composition on completion of mixing. Three numerical examples should illustrate the effects of various important parameters. For 100 kg of lead dust with 65%

TABLE 3.6. HEAT EFFECTS FOR THREE EXAMPLES GIVEN IN THE TEXT

Material	Mixture 1		Mixture 2		Mixture 3	
	Enthalpy (kJ)	Enthalpy (kJ)	Enthalpy (kJ)	Heat Capacity (kJ/°C)	Enthalpy (kJ)	Heat Capacity (kJ/°C)
Lead	5,250	5,250	5,250	3.8	5,250	3.8
Lead oxide	—	—	—	12.2	—	13.5
Lead sulfate	6,830	5,360	5,360	5.3	2,070	2.1
Water	—	—	—	87.6	—	79.0
Heat of reaction and heat capacity of the chemical components	12,080	10,610	10,610	108.9	7,320	98.4
Mechanically produced heat and heat capacity of the mixtures	1,400	1,400	1,400	15	1,400	15
Total heat and heat capacity	13.5 MJ	12.0 MJ	12.0 MJ	0.12 MJ/°C	87 MJ	0.11 MJ/°C

oxide content ( $n_1 = 169$  mole Pb and  $n_2 = 291$  mole PbO) the lead content is expected to decrease during mixing by  $\Delta n_1 = -24$  to  $n_1 = 145$ . The dust is mixed in three different acid formulations (Table 3.6).

1. With 5 kg sulfuric acid ( $n_3 = 51$ ) and 20 kg water ( $n_4 = 1.110$ ). These components are added separately as 9.57 kg = 6.78 liter of sulfuric acid ( $\rho = 1.411$ ) kg/liter and 15.43 liter of water.
2. With 5 kg sulfuric acid ( $n_3 = 51$ ) premixed with 20 kg of water. The 25 kg of the diluted acid with a density  $\rho = 1.127$  kg/liter is added.
3. With 2 kg sulfuric acid ( $n_3 = 20.4$ ) premixed with 18.4 kg of water ( $n_4 = 1.020$ ). It is added as 20.4 kg dilute acid with a density  $\rho = 1.063$  kg/liter.

Estimation of the heat generated during the mechanical mixing is generally not possible. If the mixer motor is connected to a wattmeter, an estimate of the frictional heat may be obtained. The energy consumed in operating the mixer, either empty or filled with dry dust, appears to be about the same. It contributes only slightly to heating the load and covers the transmission and bearing losses. During the actual mixing period of about 2 to 5 minutes, when the mass is still very stiff, the additional energy is converted to heat. The value decreases into a small, approximately constant value for the finished paste. A mixer with a capacity of about 600 to 700 kg of powder

TABLE 3.5. NOTATIONS FOR CALCULATIONS OF THE CHEMICAL HEAT EFFECTS OF MIXTURES OF LEAD DUST, WATER AND SULFURIC ACID: COMPOSITION IN MOLES

Material	Initial State	Change	Final State	Enthalpy (kJ)	Heat Capacity (J/°C)
Lead	$n_1$	$-\Delta n_1$	$n_1 - \Delta n_1$	$\Delta n_1 \cdot 219.0$	$26.44 \cdot (n_1 - \Delta n_1)$
Lead oxide	$n_2$	$+\Delta n_1 - n_2$	$n_2 + \Delta n_1 - n_2$	—	$45.82 \cdot (\Delta n_1 + n_2 - n_2)$
Sulfuric acid and lead sulfate	$n_3$	0	$n_3 + n_2$	$n_3 \cdot \Delta H_R$	$103.7 \cdot n_3$
Water	$n_4$	$+\Delta n_4$	$n_4 + n_2$	—	$75.29 \cdot (n_4 + n_2)$

dust may introduce work equal to 2.5 k Wh for each 600-kg load, or about 1400 kJ/100 kg of powder.

The chemically and mechanically generated heat is reduced by heat losses from

1. Vaporization of water.
2. Heat loss to the mixer and surroundings by conductance; the mixer may or may not be equipped with water or air cooling.

Chemical and mechanical heat is absorbed primarily by the mass and causes its temperature to rise, for heat conduction through the mass is minimal. Heat transfer to the mixer occurs mainly by direct contact. Temperature equilibrium can scarcely be attained in the mixing period of approximately 25 to 30 minutes. Yet a certain portion of the heat is transferred to the stirrer and a portion to the walls. Because the mass of the mixer is 200 to 250 kg, the mixer's heat capacity amounts to about 100 kJ/°C or proportionately about 15 kJ/°C for 100 kg of dust.

At the start of mixing the generated heat leads to a temperature rise in the mass accompanied by vaporization of water. The vaporization of water removes about 2400 kJ/kg of water evaporated at 45°C and a vapor pressure of water of 0.1 bar. In the evaporation of 1 liter of water/100 kg of powder the temperature lowers about 20 to 25°C (based on a heat capacity of 100 kJ/°C).

The oxidation of lead dust occurs from the very beginning of the mixing process. The reaction enthalpy of 5250 kJ/100 kg of powder could lead to a temperature rise,  $\Delta T = 50^\circ\text{C}$  (or about  $2^\circ\text{C}/\text{min}$ ), based on the estimated heat capacity of the material of about 100 kJ/°C, not considering heat transfer of the stirrer absorbs a portion. Oxidation does not occur in lead-free powders or in closed, continuously operating mixers.

If sulfuric acid is added continuously to mixtures 2 and 3 and no heat is lost to the mixer, mixture 2 is raised about  $110^\circ\text{C}$  and mixture 3, about  $90^\circ\text{C}$ . If a partial heat loss is assumed during a mixing period of 30 minutes, lower rises are estimated to be  $3.0$  to  $3.5^\circ\text{C}/\text{min}$ . In production the rise is usually less.

If during the mixing step a powder/water mixture is prepared first and the entire amount of high density acid is added within a few minutes, the temperature rise will be very rapid. For mixture 1, neglecting the oxidation of lead and without heat transfer to the mixer, a temperature rise of  $60^\circ\text{C}$  could occur in about 3 minutes. During admixing of sulfuric acid the product changes from a stiff powder/water mixture to a pasty sulfate. Because of the consumption of mechanical work required for kneading, the temperature increases above the calculated value. If equilibrium among all heat effects is attained (i.e., without additional cooling or evaporation of water), the temperature increase will still be above  $70^\circ\text{C}$ , which is usually considered to

be the critical temperature. Despite a considerable uncertainty in this estimate, we realize that mixtures with higher sulfate contents require additional cooling.

#### RHEOLOGY OF THE PREPARATION OF PASTED PLATES

The theoretical foundations were discussed in Section 2.6. The starting product for the manufacture of pasted plates is a lead dust. Its chemical composition should be considered insignificant at first. For dusts with or without lead similar observations apply with respect to mixing and curing, aside from the thorough oxidation of the metallic lead during the last stage of curing.

Lead powders are characterized by their water absorption by which the density is measured as a function of the addition of water (see Figures 2.56 to 2.58). Initially the density rises almost linearly. After a definite amount of water addition, characteristic of the powder, it rises steeply, attains a maximum, and then decreases. During this sequence the plastic state is achieved and traversed.

In the plastic range the particles are separated by a thin film of water which allows them independent movement. However, the particles must adhere to one another; therefore the water film must not be too thick. In this process an important part is assigned to the internal surface and especially to the portion of the particles sized below  $1\ \mu\text{m}$ . Systematic studies in this field are not available. Several known observations relate to the behavior of sulfate-containing mixtures (Burbank and Ritchie, 1969), during the curing and drying processes, as well as during formation. According to these results, the fine portion should be between 4 and 25%, but no studies have yet been devoted to the optimization of mixing formulations.

In Section 2.6 only mixtures of lead dust and water were discussed. The general rheological fundamentals are independent of the nature of the material. By the addition of sulfuric acid an appreciable portion of the oxide component is converted mainly into an anisotropic, needleshaped reaction product which forms slowly from the initial crystal seeds. The recrystallization continues, after mixing, during the curing process. The needle crystals make the packing bulkier. As the void volume gets larger, the strength increases. Figures 3.9 and 3.10 show the apparent density as a function of sulfate content and water addition. It is also shown that a change in the density of the solid (a function of sulfuric acid content) exerts a smaller effect on paste density than a change in the amount of water.

Figure 3.10 illustrates the dependence of the density maximum on the amount of sulfate for the two powders (1 + 2 in Figure 2.58) as well as the beginning of the plastic range. The water values of the density maxima shift to higher values with increasing sulfate content and additional amounts of

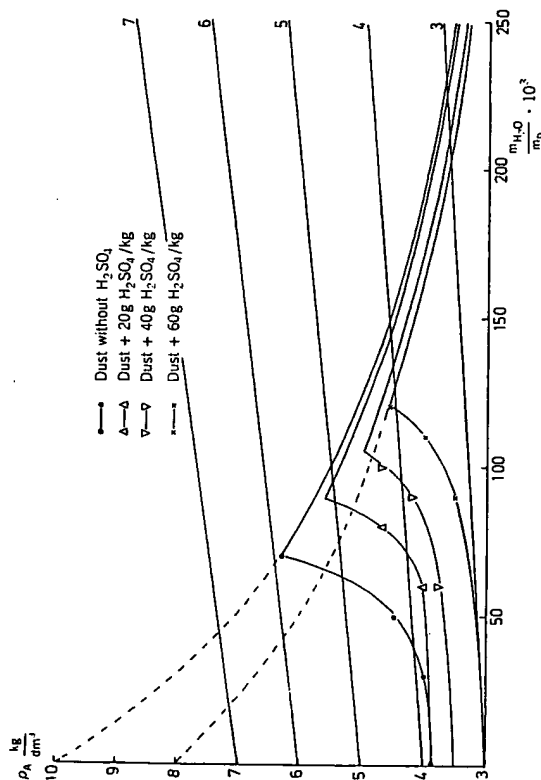


Figure 3.9 Apparent density of mill dust (I of Figure 2.58) as a function of sulfate content and water addition.

water are needed to reach the plastic states. Sekito and Ichimura (1968) showed that with other lead powders the width of the plastic range increases at low sulfate content (to about 3 to 4 kg/100 kg powder). With larger sulfate contents, that is, in pastes largely containing fibers of tribasic sulfate, the width of the plastic range becomes smaller and may completely disappear.

The preceding considerations naturally apply only if the basic sulfate forms as needles. If a strongly localized overacidification occurs, grainy normal lead sulfate is produced, a structure unfavorable to subsequent pasting.

Once a fibrous structure is obtained, it is retained in the curing process. The strength of the structure is improved because of the needle crystals. To ensure sufficient strength in the plates, synthetic fibers are often added to the highly porous active materials. In addition, tribasic sulfate increases the strength [Voss and Freundlich, patent (1965)].

During manufacture of the active materials for the negative plates, further additions are made (see Section 2.2) which may affect their rheological properties, mainly by changing surface tension and the contact angle of the organic components. There are no published data on this subject.

The pasting properties (i.e., their plastic behavior) are important in the manufacture of plates and also affect the electrochemical properties of the

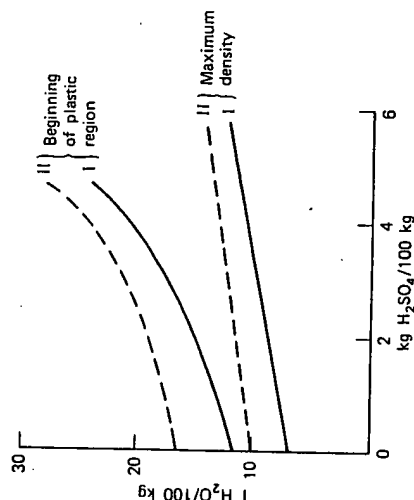


Figure 3.10 Dependence of the density maximum and beginning of the plastic range on the acid content of two mill dusts (I and II of Figure 2.58).

finished plates. During the grid loading the composition of the pastes forms the basis for the structure of plates and thereby determines the volumetric capacity.

No generalities may be made on a satisfactory paste density, for they do not unequivocally determine the behavior of the active material. However, the more porous an active mass, the larger the internal surface consequently a higher useful capacity and a better utilization is obtained. Yet the paste density or its water content is not a unique measure for the porosity, for the latter also depends on the active material structure after curing and formation. The shrinking process especially leads to different stabilities for the same paste densities that exert an effect on the life cycle.

Positive pastes with densities  $\rho_p < 3.9$  kg/liter are less suitable, for they tend to sludge. For paste densities  $\rho_p > 4.3$  kg/liter the capacities are smaller; also such dense materials often tend to warp.

Somewhat higher densities in the range  $4.2 < \rho_p < 4.9$  kg/liter are recommended for the pastes of negative active masses.

#### RHEOLOGY OF THE CURING PROCESSES

After curing crackfree drying of the plates and thorough oxidation of the residual lead should be guaranteed. During curing the paste shrinks and contracts. Because contact with the grid rods and grid frames must not be lost, controlled or linear shrinkage, called capillary shrinkage because of withdrawal of water, is desired. It should proceed as a decrease in volume without additional void formation (see Section 2.6).

To ensure drying without the formation of cracks, two steps in the process must be distinguished. In the first phase the liquid saturated paste undergoes a steady loss of water and decrease in volume so that no cracks or coarse pores form. This means that the density change must follow the same curve as the addition of water after the density maximum. If, after mixing, no additional chemical or physical changes occur in the paste, the maximum density will again be reached on completing this first phase. Because a recrystallization often occurs, a shift to smaller density values and therewith to higher porosities may be expected. At or near the maximum density is an aggregate of particles that mutually touch and support one another.

During the second phase of water removal no further volume changes may occur. The water is removed only when voids are formed. The density decreases linearly with the water content and the porosity remains constant, no matter whether or not the void space is filled with water. The mass fields are not allowed to detach from the grid. The total shrinkage should be limited to a decrease in thickness.

Table 3.7 describes the behavior of the curing process with time, during which samples were taken at about 2-hour intervals. This table describes a paste of a sulfate-containing powder whose water content at the maximum density  $V_v = 0.115$  liter/kg; the specific solid volume is  $V_s = 0.110$  liter/kg.

Table 3.7 contains the analytically determined content of metallic lead by weight (column 9), water  $V_w$  (column 3), and void volume  $V_v$  (column 2), determined from measurements with the Hg porosimeter. The decrease in interstitial volume ( $V_v + V_w$ ) is recognizable during the first phase in sample 3, the values remain constant to completion of the processes (average value, 0.126 liter/kg). For ideal shrinkage no air-filled cavity should form during the first phase; eventually the interstitial void volume associated with the maximum density, 0.115 liter/kg will be attained. As Figure 3.11a shows, the shrinkage factor (column 8) lies in the region of 1, the value for ideal shrinkage. According to the model, the removal of water from the fine pore system occurs inversely to the water take-up.

In the second phase of the process, beginning at sample 4, almost no change in total volume occurs. Usually a fine-pored cavity starts to form, as noted experimentally by the shift in the inflection point of the curves in Figure 3.11a from 3.2 to 0.3  $\mu\text{m}$ . In the logarithmic distribution curves of Figure 3.11b (for curves 6 and 8 of Figure 3.11a) show more clearly the existence of coarse and fine-pore voids.

At first the interstitial water is removed, and the residual wedge water is bound more firmly, by which a porosity extending through the entire material originates and air can penetrate in sufficient amounts through these pores.

TABLE 3.7. TIME DEPENDENCE OF THE CURING PROCESS

(1)	Test Number	(2)	Void Volume ( $V_v$ )	(3)	Water Content ( $V_w$ in $H_2O$ )	(4)	Void and $H_2O$ -Volume ( $V_v + V_w$ )	(5)	Change in Void Volume ( $\Delta V_v$ )	(6)	Change in $H_2O$ -Volume ( $\Delta V_w$ )	(7)	Change of Total Volume ( $\Delta V_t$ )	(8)	Shrinkage Factor ( $\Delta V_w/\Delta V_t$ )	(9)	Content of Metallic Pb [100 w (Pb)]	(10)	Pore Diameter $d$ ( $\mu m$ )
		Initial value	0.0	20.0	20.0														
	1		0.4	19.0	19.4			0.4	-1.0	-0.6	1.7	-4.5	-1.4	1.9	17.8	17.9	0.32		
	2		0.9	14.0	14.9			0.5	-5.0	-4.5	1.1	-4.5	-1.4	1.6	1.9	17.8	17.9	0.32	
	3		1.7	11.8	13.5			0.8	-2.2	-1.4	1.6	-4.5	-1.4	1.6	1.9	17.8	17.9	0.32	
	4		3.0	9.1	12.1			1.3	-2.7	-1.4	1.9	-4.5	-1.4	1.6	1.9	17.8	17.9	0.32	
	5		4.2	8.6	12.8			1.2	-0.5	-0.7	0.7	-4.5	-1.4	1.6	1.9	17.8	17.9	0.32	
	6		9.0	3.9	12.9			4.8	-4.7	+0.1	4.7	-4.5	-1.4	1.6	1.9	17.8	17.9	0.32	
	7		10.2	2.8	13.0			1.2	-1.1	+0.1	11	-4.5	-1.4	1.6	1.9	17.8	17.9	0.32	
	8		11.5	1.0	12.5			1.3	-1.8	-0.5	3.6	-4.5	-1.4	1.6	1.9	17.8	17.9	0.32	
	Final value		12.5					1.0	-1.0	0									

"All volumes are given in liters/100 kg, mass content in 100 w = weight %, solid volumes amount to 11 liter/100 kg."

$$S_{\text{ideal}} = \frac{20}{20 - 11.5} = 0.27; S_{\text{real}} = \frac{20}{20 - 12.6} = 0.24 \text{ (for test No. 3)}$$

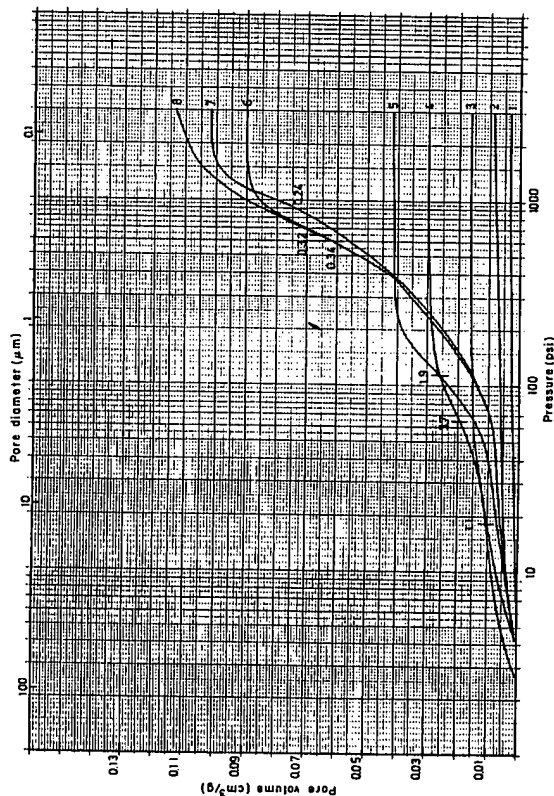


Figure 3.11a Mercury porosimeter measurements on unformed plates during the curing and drying process.

The particle surfaces are still covered with a thin film of water. Under this water film oxidation of lead occurs at a higher rate.

It is observed that the lead content decreases abruptly after sample 5 at a water content of about 8.6%. Although in this experiment a lower limit of about 10% by weight of metallic lead was reached in manufacturing, it must drop further.

According to Greenburg et al. (1951), a maximum of lead oxidation occurs at 5 to 5.5% (water, whereas Humphreys et al. (1970) give a somewhat higher value of 7.0 to 8.5% water content.

The heat generated during lead oxidation vaporizes the adsorbed and wedge water, the tightest bound portions. If the vaporization occurs too early or too rapidly, the oxidation of lead is hindered, for water is a catalyst in this process (see section 2.1). The temperature rise indicates the end of the curing processes. The dissolved material (also lead oxide) concentrates in the wedge water and deposits as a cement on the contact points of the particles. Newly precipitated lead oxide strengthens the network of needles which raises the dry strength of the plates.

The manufacture of crackfree plates is safest if the shrinkage is small, everything else being equal. On the other hand, there must be enough water

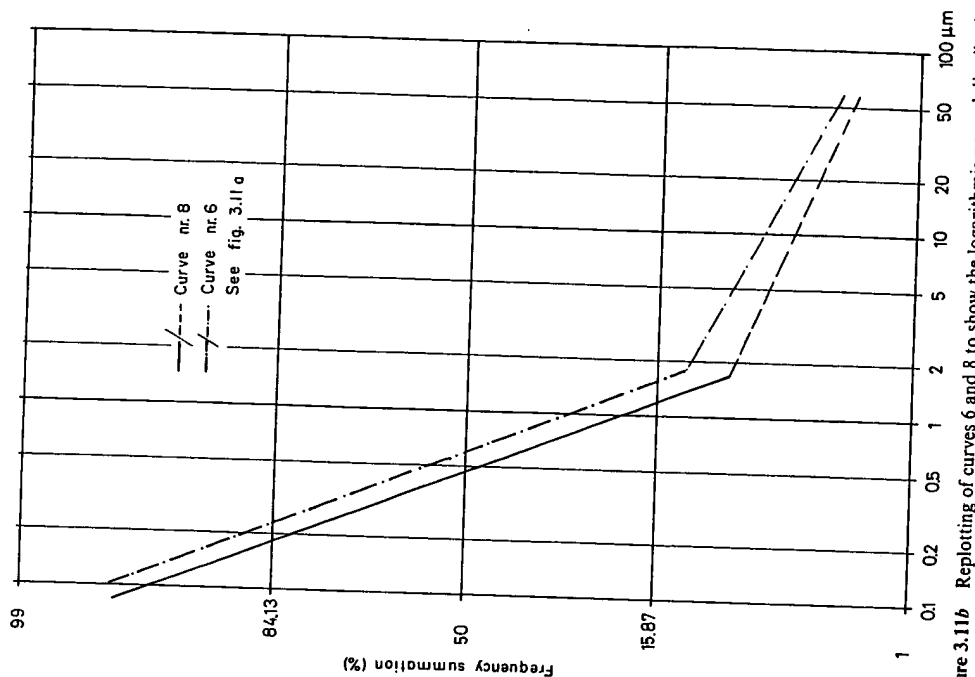


Figure 3.11b Replotting of curves 6 and 8 to show the logarithmic normal distribution.

present so that the material can be pasted and loaded in the grid and to give the plates enough porosity. Therefore the following conditions apply:

1. A lead powder is used with a high water value at the density maximum.
2. This value may be increased by the addition of sulfuric acid.
3. The water content is held as low as is compatible with the production techniques.

The first and third conditions are based on the characteristics of the dust. They are dependent on particle size distribution, shape, and internal surface. The second requirement is freely chosen for dusts within a certain range.

As a numerical example, Table 3.8 describes the behavior of a special lead dust. Its water absorption is given Figure 3.9. This dust has a water value of 0.10 liter/kg at maximum density. It was mixed in two sets of experiments:

1. At constant water content with variable amounts of sulfuric acid.
2. At constant sulfuric acid content with variable amounts of water.

The pasted grids are treated under constant conditions (15 hours in a humid atmosphere, followed by two days of air drying). Table 3.8 is a summary of paste properties as a function of water and sulfuric acid content.

1. The paste density is almost entirely independent of sulfuric acid content but is strongly affected by water content; see columns 4 and 5 in Table 3.8.
2. The solid volume changes only slightly with the sulfate content; see column 6 in Table 3.8 (on oxidation of lead from  $W(\text{Pb}) = 0.30$  to  $<0.05$ , the volume increased by about  $\Delta V_s = 0.01$ ).
3. The void formation during the curing process depends on the water content of the paste for equal working conditions; compare columns 1 and 7 in Table 3.8.
4. The more the water content of the paste exceeds the value  $V_{\text{max}}$ , the greater the tendency to form large pores and cracks [real or irregular shrinkage, column 9 compared with the ideal value in column 10].
5. In manufacturing the volume changes during shrinkage are essentially determined by the technology of the curing processes. Thus the total volume change (column 8) for the pastes of like water content ( $W = 0.2$ ) is the same ( $\Delta V_4 = 0.058 \pm 0.002$ ), for they are worked under the same conditions. Mixtures that approach the ideal shrinkage show the largest value of maximum density.

Column 12 in Table 3.8 lists the relative portion of irregular shrinkage of the plates' total pore volume. The trend confirms the assumptions. Specifically, the numerical values apply only to a particular paste and to a definite curing and drying program. The quantitative behavior depends, among other factors, on the plate's thickness, temperature, and the moisture content in the manufacturing machines. Deviations may be caused by increasing the volume of the solid as a result of the oxidation of lead and the change in the fiber structure induced by recrystallization.

The curing process can be carried out by diversified methods, but several generalities must be considered. The first phase of the shrinkage in volume

TABLE 3.8. DEPENDENCE OF SHRINKAGE OF A LEAD DUST PASTE ON WATER AND ACID CONTENT<sup>a</sup>

(1)	Water Content (%)	(2)	$\text{H}_2\text{SO}_4$ g/kg Pb-Dust	(3)	Water Value at Maximum Density (liter/kg)	(4)	Paste Density (kg/liter)	(5)	Solid Volume <sup>b</sup> (liter/kg)	(6)	Void Volume <sup>b</sup> (liter/kg)	(7)	Change in Total Volume <sup>b</sup> ( $\Delta V_4$ ) (liter/kg)	(8)	Shrinkage (vol %) $S_{\text{ideal}}$	(9)	$V_r - V_{\text{max}}$	(10)	$V_r - V_{\text{max}}$	(11)	$V_r - V_{\text{max}}$	(12)	$V_r - V_{\text{max}}$
20	0		0.100	4.10	3.98	0.102	0.108	0.110	0.144	0.055	0.182	33.1	0.045	18.2	19.2	30.1	0.039	0.031	0.21	0.25	0.09	0.07	0.03
20	0.02		0.114	4.09	3.97	0.110	0.141	0.059	0.056	0.055	18.2	27.9	0.030	0.021	18.1	21.2	0.010	0.013	0.21	0.25	0.09	0.07	0.03
20	0.04		0.120	4.05	3.97	0.113	0.139	0.061	0.043	0.057	18.1	23.6	0.013	0.004	18.1	21.2	0.010	0.010	0.21	0.25	0.09	0.07	0.03
20	0.05		0.133	4.05	3.96	0.115	0.137	0.061	0.043	0.057	18.1	23.6	0.013	0.004	18.1	21.2	0.010	0.010	0.21	0.25	0.09	0.07	0.03
20	0.05		0.133	4.05	3.96	0.115	0.143	0.057	0.043	0.057	18.1	23.6	0.013	0.004	18.1	21.2	0.010	0.010	0.21	0.25	0.09	0.07	0.03
20	0.05		0.133	4.05	3.96	0.115	0.143	0.057	0.043	0.057	18.1	23.6	0.013	0.004	18.1	21.2	0.010	0.010	0.21	0.25	0.09	0.07	0.03
22	0.05		0.133	3.83	3.79	0.115	0.162	0.058	0.058	0.068	17.3	26.0	0.029	0.018	17.3	26.0	0.029	0.029	0.18	0.21	0.07	0.03	0.03
24	0.05		0.133	3.65	3.63	0.115	0.172	0.068	0.068	0.068	19.2	30.1	0.039	0.031	19.2	30.1	0.039	0.039	0.23	0.25	0.09	0.07	0.03

<sup>a</sup> See Figure 3.9:  $V_{\text{max}}$  = maximum density. Initial value with  $W(\text{Pb}_{\text{net}}) = 0.30$ ; final value after oxidation  $W(\text{Pb}_{\text{net}}) < 0.05$ .



should occur during not too rapid drying in a damp atmosphere (vapor pressure slightly less than the vapor pressure of the water in the paste) at a low temperature (below 70°C). In the second phase drying should be completed without a change in volume.

The mixing and curing processes are important because they control the physical structure of the finished plates. The development of a compact structure is determined by kneading the mixture. Experimentally, the compact structure corresponds to maximum density, a coordination number of about 7, and between 40 and 60% porosity.

On transition from the maximum density to the plastic state, the particles are separated by a thin film of water without any appreciable change in structure. In the reverse process for removing water the same compact structure should be attained. This structure corresponds to maximum density and can be characterized by *maximum shrinkage*. Thus crackfree drying is accomplished and the plates possess a void volume with fine pores and a large internal surface.

#### OTHER COMPONENTS OF ACTIVE MASSES

The life and capacity of electrodes depends not only on the lead-containing components discussed in the preceding sections but also on other materials added deliberately or accidentally to the active materials of the plates.

The desired additives include expanders in the negative active material and fibers to raise the strength. The addition of phosphoric acid to the paste or electrolyte (see Section 2.1) leads to an increase in life by hardening the active mass but to a loss of capacity (Kugel, 1926/1929) and added difficulties if used at a low temperature. Other substances could be formed during battery use by dissolving impurities or alloy constituents in the grids, the antimony compounds in particular.

A third group contains a series of materials added to the electrolytes which somehow influences the behavior of the active masses of the electrodes—"secret substances" that are supposed to improve sulfated batteries. In many cases their action is disputed, often called worthless, and may even be harmful. A discussion of these materials is not provided here.

Characteristic of all these additions to the active materials is their use at low concentrations. They do not participate stoichiometrically in the electrochemical reactions but act as catalysts or inhibitors, mainly by changing the absorptive properties and structure of the electrical double layer.

#### Antimony

Cells with hard lead grids show the effect of antimony. Lead powder, however, also contains small amounts of antimony (about 10 to 100 ppm).

Therefore absolutely antimony-free cells are never encountered. The antimony content of lead dust occurs as an impurity in pure lead and accelerates the oxidation of lead in the mills and the Barton process.

During formation relatively large amounts of antimony dissolve from the positives (0.15% of the total antimony dissolves in 45 hours), whereas a small amount dissolves out of the negative grids, and only near completion of the formation (less than 0.01%). Formation was carried out with  $\rho = 1.09$  kg/liter and  $i = 0.35$  A/dm<sup>2</sup> of plates with hard lead grids (antimony content, 8%). Antimony was determined with radioactive <sup>124</sup>Sb. Most of the antimony is reprecipitated in the positive active material (0.13% based on the total active material), less in the negative plate (0.01% based on the active material); (see Hermann et al., 1957/1958).

On continuous charge (300 hr at 0.6 A/dm<sup>2</sup>) dissolved antimony rises to 6%. The same value is attained on cycle life test (discharge 1 hr at 1.8 A/dm<sup>2</sup>, charge 5 hr at 0.4 A/dm<sup>2</sup>, 100 charge/discharge cycles). The largest part is always deposited in the positive active material (up to 0.5%), and only about 0.03% in the negative active material (depending on cycling activity) but up to 1.2% on the overcharge test. The electrolyte may contain 3 to 15 mg/liter.

In the overcharging test the possibility of forming SbH<sub>3</sub> (based on the same amount of current under comparable conditions) appears to be greater than in the cycling test. Here, too, antimony is found mainly in the positive active material (up to 0.5%) (Zehender et al., 1964).

If antimony (as Sb<sub>2</sub>O<sub>3</sub>) is added in larger amounts (up to 10%) to lead dust, the oxidation of metallic lead is almost entirely prevented during the curing process (Ritchie, 1952).

The inhibiting action appears to be complex, for antimony is found in all states of oxidation, Sb<sup>v</sup>, Sb<sup>iii</sup>, and Sb<sup>o</sup>. The purpose of adding antimony oxide is related to the decreased life of plates with antimony-free grids. In particular, the sludging of the positives increases. Also, the difficulties that occur during curing make it unlikely that antimony in the grid will be replaced by the addition of oxide as long as metallic lead-containing dusts are used.

The electrochemical behavior of antimony in relation to the acidity and valence states is shown in Table 3.9 (see also Dawson et al, 1971). If metallic antimony is charged anodically in a sulfuric acid solution (without complex-forming components), starting from the potential of the standard hydrogen electrode, trioxide will form first. The pentoxide then forms with further rising potential. If these oxides are present as precipitates, the concentrations of the dissolved antimony are fixed. In solution we find trivalent antimony as antimonyl (III) ion (SbO)<sup>+</sup> and undissolved antimony (III) acid (HSbO<sub>2</sub>). The pentavalent antimony (V) occurs as (SbO<sub>2</sub>)<sup>+</sup> and the antimonic (SbO<sub>3</sub>)<sup>-</sup>.